JANUARY 1960
Volume 14, Number 1

FT food technology

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answer . . . page 4

THE JOURNAL OF THE INSTITUTE OF FOOD TECHNOLOGISTS

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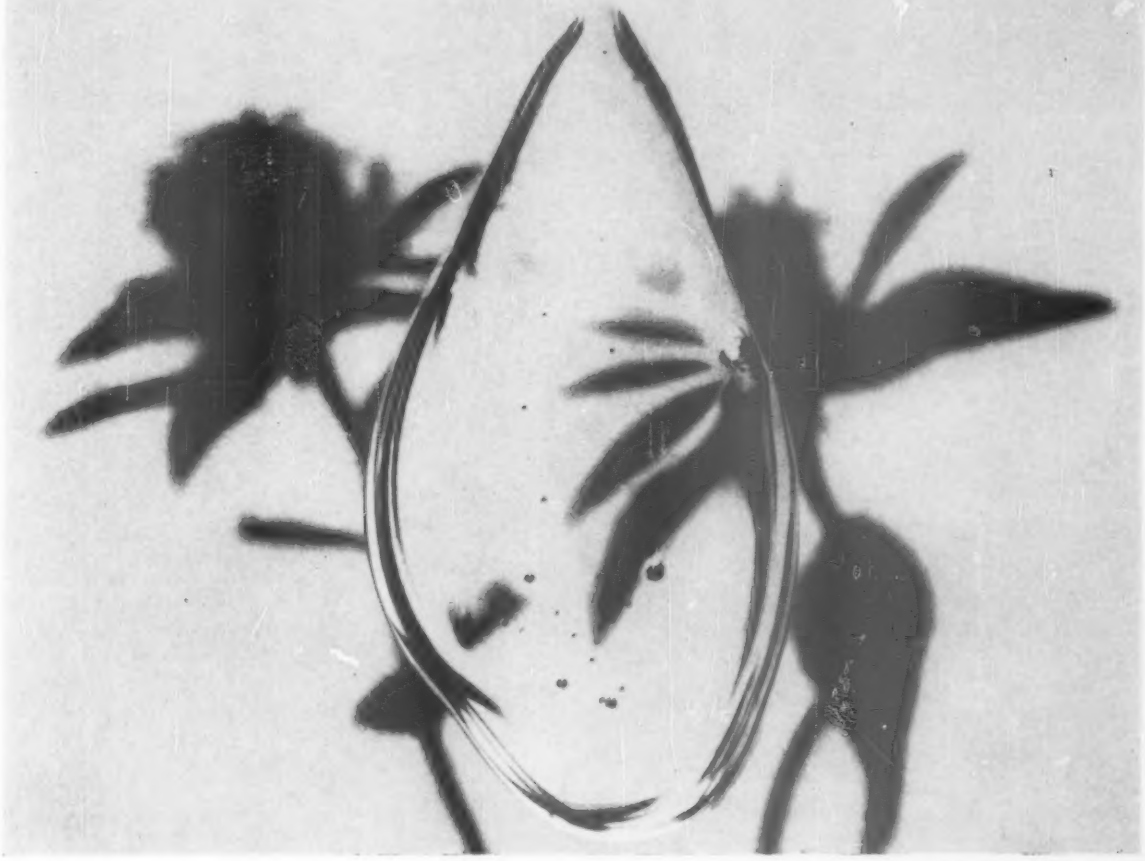

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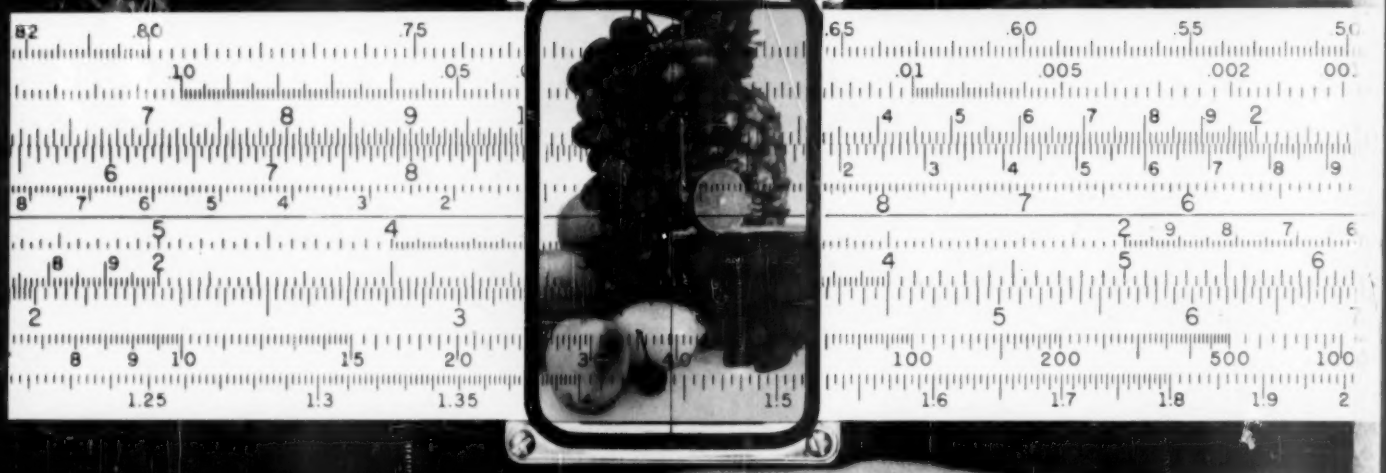

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FT food technology

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Consider now, who you feel should receive these funds. Only thirteen persons in the United States and Canada will be selected.

Purpose of expenditure of these monies is to encourage:

- —graduate work in the field of food science
- —graduate work in the field of science with particular emphasis on its relation to foods
- —graduate work in the fields of food science and food technology
- —deserving and outstanding students to take undergraduate work leading to a Bachelor's Degree in Food Technology, Food Engineering or Food Science.

Anyone Can Help

Furtherance of educational standards in the United States is one reason the IFT administers Fellowships, Scholarships, and Awards. You, member or not, can help in this administration by bringing these awards to the attention of students who you feel may qualify. Support your organization as it attempts to do its part in maintaining and raising U. S. educational standards.

A $1000 Florasynth Fellowship is administered each year. It is awarded to a B.Sc. candidate who has a better than average scholastic record, and who is engaged or plans to engage in graduate work for an advanced degree in one of the fields listed above. In addition, the awardee shall receive an engrossed plaque.

IFT'ers Important

Each of the other twelve individuals receiving an award must make his own application. This is where Institute members are extremely important. Try to ensure that all qualified students in your area are aware of the possibility of receiving financial aid toward their education. Most members probably realize the significance of such aid to a student and potential member of the Institute.

Twelve thousand dollars is donated annually by the General Foods Fund, Inc., in the form of three General Foods Fellowships at $4,000 each, with an engrossed plaque to each awardee. Fellowships will be awarded to deserving and outstanding United States or Canadian citizens, engaged in senior undergraduate or graduate work in recognized educational or research institutions in the United States of America or Canada, and who propose to pursue graduate work in basic or applied chemistry, chemical engineering or related sciences, which may involve new physical or other procedures, directed to extending or improving knowledge in some phase of food conservation, food production or food processing, rather than primarily for research in the fields of nutrition, bacteriology or analytical chemistry.

Tell Students This . . .

Tell students they are responsible for submitting their own letter-form application in applying for the General Foods Fellowships.

The applicant shall have an approved plan of research and acceptance thereof by the Graduate School of the institution in which he proposes to hold the Fellowship. In presenting his application, the applicant should indicate his definite intentions on his word as a gentleman, to carry through with his approved research plan for the period of time for which the award is made insofar as it is humanly possible.

The other Fellowship, of which your Institute is administrator and donor, is the Samuel Cate Prescott Fellowship. An engrossed plaque and $1,000 is awarded annually to the student selected, who meets the following general conditions: the award will be made annually to an outstanding young man or woman of any nationality engaged in senior undergraduate or first year graduate work in the general field of food science and food technology, at a recognized educational or research institution in the United States or Canada.

Again the Institute relies on its members to disseminate information to students that they are responsible for submitting applications.

DEADLINE for receipt of all Fellowship nominations and applications will be strictly adhered to this year. The date is March 1, 1960.

Eight thousand dollars worth of undergraduate awards and scholarships valued at one thousand dollars each, will be made this year, with Gerber Baby Foods Fund, Inc. donating six. Dodge and Olcott, Inc. will donate one such scholarship, as will the F. Ritter & Co. Accompanying these awards will be an engrossed plaque for each awardee.

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Qualifications for each of the undergraduate awards and scholarships are similar, viz.: an applicant to qualify must have satisfactorily completed, prior to the effective date of the award, two full years of college work that will adequately prepare a student to complete the Junior and Senior years of a Food Technology course that is the equivalent of the model curriculum approved by the Institute of Food Technologists (see FOOD TECHNOLOGY, Vol. 12, No. 9, 1958). Candidates will be judged on over-all ability including scholarship, personality, extra curricular activities, social adjustment, character, etc.

So beat the deadline, March 1, 1960, by which time all applications and nominations for all awards must be received. Submit to Executive Secretary, Institute of Food Technologists, 176 W. Adams Street, Chicago 3, Illinois, along with any questions or correspondence.

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IN THIS ISSUE—

THE TECHNICAL ARTICLES IN BRIEF

Peeling method *Potatoes*

Lye-pressure steam peeling of potatoes and other products. Harold W. Adams, Frank D. Hickey, and Miles J. Willard, Jr.

Whether a mechanical lye peeler or a steam peeler is used—each has its limitations. However, a comparatively new method, pre-coating products with hot caustic solution, and then subjecting them to atmospheric steam under pressure, has been shown to offer greater flexibility than other techniques, and better process control. This paper presents the advantages of such a system—comparing its labor saving, yield, and flexibility of application against the same factors when steam or lye alone is used. Since processors are becoming more and more cognizant of the costs of operation and yield, the concepts introduced here should be of much interest. Also studied were the holding times in lye and steam in order to determine peel loss and peeling efficiency. Correlation of surface area to peel loss was studied, using Idaho potatoes. As surface areas increase, peel loss is decreased. Five per cent lye followed by 45 seconds at 75 p.s.i.g. steam resulted in good peeling, the peel loss being 14.6%. Addition of a wetting agent to 5% lye, followed by steam, produced good results with high yield. Cost analyses on three peeling methods indicated lye plus steam is the most economical method of peeling. (See page 1.)

Quality evaluation *Grain- vs. grass-finished beef*

The quality of grain-finished and grass-finished beef as affected by ripening. Bernadine Meyer, Juanita Thomas, Ruth Buckley, and J. W. Cole.

Feed management and ripening are two of many interacting factors affecting the quality of beef as judged by producer, packer, and consumer. Ripening up to a certain point improves the eating qualities of beef, but the effects of specific feeding regimes do not seem so clearly defined. Thinking differs as to the merits of grass-finishing versus grain-finishing in preparing beef for market. The popular opinion seems to be that grain-fed beef is superior to grass-fed. The purpose of the work reported here was to test the effects of limited and extensive ripening on the palatability of beef from grain-finished and grass-finished steers. Other conditions which might affect palatability factors were controlled as far as possible. Effects of 2, 7, 21, and 42 days of ripening on the palatability of grain-finished and grass-finished beef were studied. Medium-done loin roasts cooked by dry heat, and well-done round roasts cooked by moist heat were tested by a sensory-difference panel for tenderness, flavor of lean, flavor of fat, and juiciness. Objective estimates of tenderness were made with a Warner-Bratzler mechanical shear. Cooking losses were determined. The grain-finished beef was scored significantly higher than the grass-finished beef for tenderness, flavor of lean, flavor of fat, and juiciness. Tenderness differences due to feeding regimes were not significant when measured by shear machine. There were no significant differences in cooking losses attributable to feed. Both types of beef exhibited highly significant increases in tenderness due to ripening, but relatively more improvement was shown by the grass-finished beef. The flavor of lean of the grain-finished beef tended to improve up to 21 days of ripening, but the flavor of lean of the grass-finished beef showed little or no improvement during ripening. After 21 days, the scores for flavor of lean decreased significantly. Flavor of fat of both types of beef was significantly impaired with 21 and 42 days of ripening. Some evidence was obtained that free fatty acid developed between 21 and 42 days of ripening. Juiciness was not significantly affected by ripening. There were highly significant increases in drip losses and total cooking losses due to ripening, but evaporation losses were unaffected. (See page 4.)

Product improvement *Precooked freeze-dried ham*

Improving the stability and acceptability of precooked freeze-dried ham. A. F. Anglemier, David C. Crawford, and H. W. Schultz.

It was hypothesized that the curing ingredients of commercially cured hams were responsible for certain adverse changes that occur in freeze-drying this product. Experiments were designed in which curing methods, alteration and substitution of curing ingredients, time and temperature of curing, and precooking conditions were modified in an attempt to increase the storage stability. Results of these investigations and those obtained by the use of various stabilizers and of a long term storage study are reported. They show that packaging the freeze-dried product in vacuumized cans is superior to packaging in cans filled with nitrogen or carbon dioxide. Flavor panel results indicate that vacuum packed samples retained their acceptability for 5½ months when stored at 70° or 100° F. Use of stabilizers (that is, those tested) appears to have little effect on prolonging the storage stability of freeze-dried ham. Rehydration results of different freeze-dried ham muscles indicate that the muscles do not possess an equal water absorption capacity. The knuckle or tip muscles show the highest level of rehydration. Rehydratability is also affected by the muscle fiber orientation. Freeze-dried samples having the muscle fibers in a perpendicular position to the largest surface area absorbed more water and were rated juicier than samples having parallel fibers. Experiments were conducted in which (a) curing methods, (b) alteration and substitution of curing ingredients, (c) time and temperature of curing and (d) precooking conditions were modified in an attempt to produce a ham possessing superior qualities to obtain freeze-dried samples having excellent storage stability properties. Results of these investigations failed to show increased stability beyond that which may be obtained

JANUARY COVER. The cover for January emphasizes the Scholarship and Fellowship Award program administered by the Institute of Food Technologists. The details regarding the awards and how you can help the program achieve its goals are to be found on page 4.

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with commercially cured hams used in these studies. Deterioration of freeze-dried ham during storage reflects directly upon the acceptability of the product. Color and flavor are the quality factors most adversely affected by storage at elevated temperatures. Stability of the stored samples is also affected by the moisture level. A combination of high moisture content and high storage temperature produced the most detrimental changes. (See page 8.)

Gas chromatography — *Gases in headspace of cans*

A gas chromatographic method for determining gases in the headspace of cans and flexible packages. William H. Stahl, William A. Voelker, and James H. Sullivan.

Utilizing inert gases for the prevention of quality deterioration in packaged foods has been practiced successfully for many years. Although it is generally agreed that the determination of the concentration of these gases is of extreme importance, no practical methods are available which encompass the wide range of packages encountered. As is commonly known, the orsat method, generally used throughout the food industry, requires a large volume of sample, is time-consuming, and, when reduced to a micro scale, becomes extremely complicated. Commercial oxygen analyzers require smaller sample volumes, but are limited to the analysis of oxygen. Gas chromatographic methods, however, require less than 1 ml. of gas for satisfactory analysis, are extremely rapid, and quite versatile. The procedure used successfully for several months by the authors of this article employs a simple sampling method which can be adapted to any container, followed by gas chromatographic analysis. The method allows analysis on not more than 0.5 ml. of gas, requires 7 minutes per determination, can be run by a technician, and is sufficiently accurate for the purpose intended. (See page 14.)

Quality evaluation — *Tomato juice color*

Derivation of a new formula for computing raw tomato juice color from objective color measurement. John N. Yeatman, Arthur P. Sidwell, and Karl H. Norris.

Since color is probably the most useful single criterion for evaluating the quality of tomato fruit for processing, an accurate determination of the color of the fruit or a puree made therefrom is of prime benefit in assigning a quality grade. Any tomato-color index that may be adopted for general use should be sufficiently versatile to indicate differences between samples of purees derived from fruits ripened under a wide variety of conditions which cause substantial differences in color specification. The derivation of a new formula for computing raw tomato juice color, its development and substantiating theory, is the subject of this paper. Carefully prepared Munsell disks having regularly spaced color attributes of hue, lightness and saturation in the region of raw tomato juice colors were used by trained observers as guides in visual scoring of the samples. Visual color scores and instrument evaluations were determined for juice samples covering a wide gamut of color in Hunter-Munsell color space. Only when the 3-dimensional positions of the color readings of the juice samples in this system were visualized in relationship to the color scores, did it become possible to derive the formula which would best relate instrument evaluations with visual color scores. The empirical formula

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$\frac{2000 \cos \theta}{L}$, named the T.C. index, computed from objective color measurement of a wide gamut of samples in the region of tomato color in Hunter-Munsell color space, was found to weight appropriately the Hunter color values to correlate best with visual scores assigned by trained observers. A rugged tristimulus photoelectric instrument has been constructed to measure the designated T.C. index. (See page 16.)

Microbiology — *Spoilage bacteria on chilled poultry*

Microorganisms associated with spoilage of refrigerated poultry. Charles W. Nagel, Kenneth L. Simpson, Henry Ng, Reese H. Vaughn, and George F. Stewart.

The investigation reported here was undertaken to determine the types of bacteria associated with the spoilage of chilled poultry under present conditions of processing and marketing, as well as the possible influence of geographical location of processing facilities, location of cutting-up operations, and the use of antibiotics. One hundred and three cultures were isolated from chilled, cut-up fryers which had been allowed to spoil at 4.4° C. (40° F.). Eighty-eight of the cultures were allocated to the genus *Pseudomonas*. Two additional cultures were classified as members of the genus *Aeromonas*. The remaining thirteen cultures were assigned to the *Achromobacter-Alcaligenes* group without any attempt being made to place them specifically in either genus. The use of oxytetracycline as an aid in more precise classification of the *Pseudomonas* species from spoiled poultry was found to be of little value. Penicillin sensitivity also was not completely reliable for differentiation between the *Achromobacter-Alcaligenes* group and members of the genus *Pseudomonas*. The geographical location of processing facilities, location of cutting-up operations, and the use of antibiotics had no influence on the distribution of genera of spoilage oraginsms investigated in this study. (See page 21.)

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Radiation preservation — *Milk*

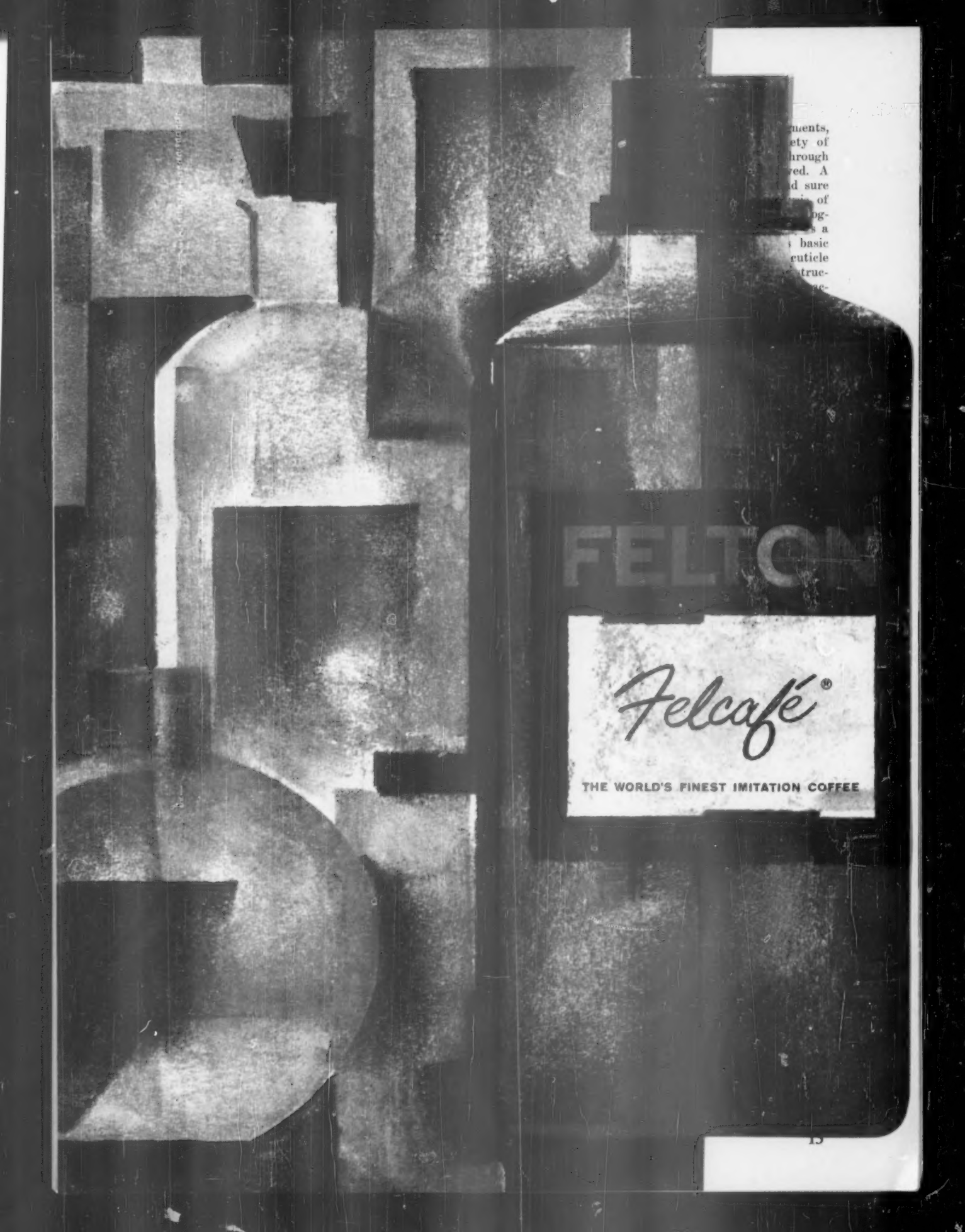
Radiation preservation of milk. X. Studies on the radiation induced gelation of concentrated milk. Methods, and effect of some additives. J. E. Hoff, J. Sunyach, B. E. Proctor, and S. A. Goldblith.

Storage studies have shown that concentrated, irradiated milk stored at room temperature or higher has a marked tendency to gel. In milk of normal concentration, or in concentrated milk stored under refrigeration, gelation is not so apparent. Preliminary studies indicated that the addition of different inorganic salts to milk had a noticeable effect on the "gelling time" of milk in storage. It was, therefore, believed that a systematic study of such additives might yield information leading to a reduction or elimination of the problem of gelation. Whether the gelation of irradiated milk bears any relation to the gelation phenomena observed in heat-processed milk was also of interest. This paper describes the methods used in the study of radiation-induced gelation and the effect of some additives. A method was devised whereby irradiation induced gelation of concentrated milk could be studied. The addition of 20 milliequivalents of Mn^{++} per liter of concentrated milk (3:1) totally prevented gelation within the experimental period (60 days). The formation of a gel during storage at 37° C. was considerably delayed by the addition of the divalent cations, Mg^{++} and Mn^{++}, whereas Ca^{++} had no effect. Phosphate and citrate were found to enhance gelation. When the gelation of the irradiated milk was induced by heating at 90° C., Ca^{++} addition effected an increase in gel strength, whereas citrate and phosphate reduced the gel strength. No significant change in gelling time was observed under these conditions. On the basis of the experimental observations it is suggested that irradiation causes the rupture of pyrophosphate linkages essential to the stability of the casein micelles. (See page 24.)

Radiation preservation — *Milk*

Radiation preservation of milk. XI. Studies on the radiation-induced gelation of concentrated milk. The effect of polyphosphates. J. E. Hoff, J. Sunyach, B. E. Proctor, and S. A. Goldblith.

Addition of polyphosphates to concentrated (3:1) milk before irradiation markedly reduces the tendency of irradiated milk to develop a gel when stored at 37° C. ATP, tripolyphosphate and "hexametaphosphate" prevented gel formation for an undetermined length of time in excess of two months at 37° C. when added in amounts above a certain threshold value specific for each compound. Pyrophosphate did not exhibit this phenomenon. The analysis of ultrafiltrates of irradiated milk demonstrated that the irradiation caused a release of Ca^{++}, Mg^{++} and phosphate ions from complexing with the casein. Addition of tripolyphosphate to irradiated milk caused an increased complexing of these ions with casein. Nearly all the added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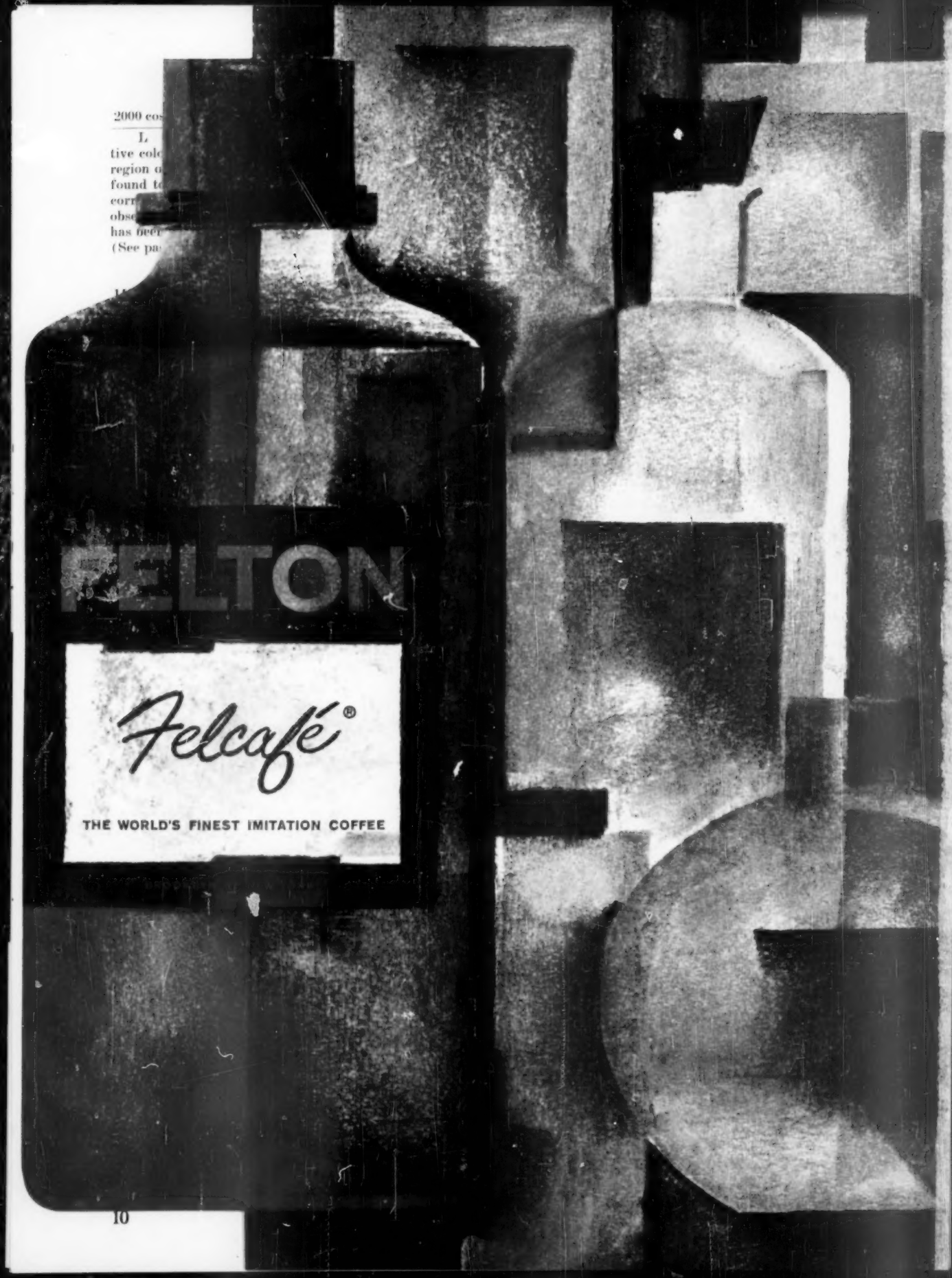
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tripolyphosphate was found to complex with the protein. Irradiation of milk with added tripolyphosphate did not affect the metal-protein complex, but did result in a release of inorganic orthophosphate and other phosphates from the casein complex. The experimental results are discussed and an interpretation of the effects of irradiation and of the addition of metal ions and polyphosphate is attempted. (See page 27.)

Wine technology — *Changes in volatile components*

Changes in volatile constituents during the baking of sherry wine by the Tressler process. Leonard R. Mattick, and Willard B. Robinson.

Most of the sherry wine produced in New York State is made by the Tressler Baking Process. Introduced in 1938, the method has since been adopted as standard procedure by the wine industry in this State. The process is well adapted to use with Concord and other Labrusca-type grapes, since the strong "foxy" odor and bright red color, objectionable qualities in a sherry wine, are eliminated in a relatively short time. Thus, an excellent quality sherry can be produced more quickly at less expense. In this study, wines prepared from Concord and Niagara grapes were processed into sherry wine by the Tressler baking process. Changes occurring in the volatile carbonyl, ester and acid content were followed through the baking process. The major volatile carbonyl compound was isolated and identified as acetaldehyde. Slight traces of acetone and hexaldehyde were also present. The major volatile acids were tentatively identified as formic and acetic acids. Propionic and lactic acids were found in trace amounts. During the baking process, the volatile carbonyl and acid content increased at a rapid rate in the Concord wine. A similar increase was noted in the Niagara wine except the rate of production was approximately one-half that of the Concord. The non-enzymatic browning reaction is advanced as a possible mechanism for the formation of these compounds. Comparison bakings of Concord wine neutralized to 0.45% acid and of Concord and Niagara wines not neutralized before baking were performed to determine the effect of the presence of alkaline salts in wine during baking on the volatile acid and carbonyl production. The volatile carbonyl content of the Niagara and the non-neutralized Concord wines increased at approximately the same rate, while the rate of increase of the volatile acid content of the Concord wines both neutralized and non-neutralized were similar. These data further confirm the role of the browning reaction in the processing of sherry wine by the baking process. Of the volatiles measured, the esters increased the least in any group. The ester increase in the Niagara wine was greater than in the Concord. The ester content of the Concord wine appeared to remain unchanged after eight months' storage; however, those of the Niagara gave a significant decrease after eight months' storage. No explanation of this decrease can be advanced at the present time. No appreciable change after eight months' storage was noted in the volatile carbonyl or acid content in either the Concord or Niagara wines. (See page 30.)

Food and drug control — *Sanitation analysis*

Diagnostic sanitation analyses in food and drug control. Kenton L. Harris, and O'Dean L. Kurtz.

Principal emphasis in this paper is on the identification of insect fragments in foods and food particles. It is proposed that the analyst learn to identify insect fragments, not by attempting to recognize the infinite variety of sizes, shapes and forms in which they appear but through a study of the insects from which they were derived. A knowledge of the insect is a simple, organized, and sure key to the recognition of insect fragments. Analysis of insect fragments is facilitated, for example, by recognizing the leg as an insect appendage and the coxa, as a basic leg component. Fragmentation beyond this basic unit naturally results in variously shaped pieces of cuticle which bear little over-all resemblance to the intact structure, but which still retain the *micro*-morphological characteristics which exist on the structure itself. There are many morphological details which are considerably more complex, but the concept embracing this approach to insect fragment work is relatively simple. It is based on a tangible systematically organized foundation, the insect, with each fragment situation depending only on the insect or insects which concern the particular food field. When the analyst knows the insect he can diagnose the etiology of the contamination and so interpret its significance. (See page 33.)

Method for protecting tin-plate surfaces — *Protective films*

The stabilizing of tin-plate surfaces. R. A. Neish, and J. G. Donelson.

The oxide film normally present on tin, although protective to some degree, readily grows to such an extent that discoloration of the surface is easily discernible. This oxida-

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tion and the accompanying discoloration, commonly called "yellow-stain," can occur during storage in warehouses under humid conditions or during the baking operation that follows lacquering or enameling. However, it is not only the change in the appearance of the tin plate that is objectionable; the oxide film formed during warehouse storage can prevent the proper adherence of some lacquers and lithographing inks to the tin surface, and can cause difficulty during modern, high-speed soldering operations in the manufacture of cans. Treatments to minimize baking discoloration and warehouse deterioration of tin-plate surfaces were investigated. Several reagents were found to be effective for this purpose. Of these, sodium dichromate was the most practical for commercial use. However, the protection obtained is limited if the normal air-formed oxide lies beneath the protective film. Therefore, it is desirable to remove the existing oxide and then replace it with the protective film. This is best accomplished by cathodic reduction in the passivating solution followed by chemical or electrochemical oxidation in the presence of the passivating agent. Protective films formed on tin plate by either of these methods, though invisible and very small in thickness, provide an effective barrier between metal and oxygen. Films formed by the electrochemical reduction and reoxidation method, however, are more stable, more resistant to sulfide staining, and more resistant to attack by dilute reagents. On the other hand, films formed by this method are not entirely satisfactory with a few lacquers used by the can industry. Although research is continuing in an attempt to produce protective films that are satisfactory with all tin-plate lacquers, it is hoped that new lacquers may be developed that will permit utilization of the protective films most resistant to oxidation. (See page 37.)

Tenderness *Turkey meat*

Relationships between pH, tenderness, and moisture levels during early post-mortem aging of turkey meat. J. W. Dodge, and W. J. Stadelman.

A series of experiments was designed to investigate the tenderness problem further and attempt to discover why cooler temperatures and aging in water produce more rapid tenderization. Attempts were made to find out what relationships existed between pH, total and free moisture levels in the meat and tenderness. Turkeys were used in these experiments because of the larger number of samples obtainable from one carcass. Water uptake and rates of cooling were not shown to affect tenderness, whereas dehydration on hot carcasses was found to produce a toughening effect which could not be aged out of the meat. Tenderization during early post-mortem periods was found to be closely associated with pH. Total moisture content of the moisture in the meat was found to be associated with pH tissue did not appear to be associated with water uptake, nor was it shown to be related to tenderness. Per cent free in one instance, but for the post-mortem period studied it did not appear to be related to tenderness. (See page 43.)

Enzymology *Relation of anthocyanase to scald*

Anthocyanase activity and its possible relation to scald in sour cherries. A. C. Wagenknecht, D. M. Scheiner, and J. P. Van Buren.

Scald of sour cherries has been shown to be caused by a combination of bruising and time-temperature effects re-

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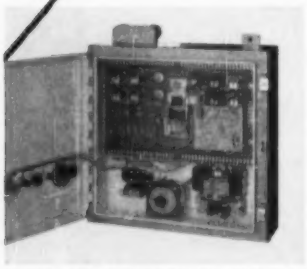

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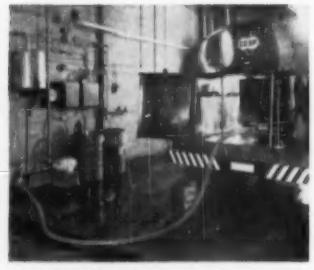

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lated to picking, transportation, and other pre-processing conditions. This phenomenon is characterized by a migration of the red anthocyanin pigment from the skin into the flesh of the fruit, followed in turn by the loss of the pigment and the appearance of a brown discoloration. This report is concerned with an enzyme system in sour cherries capable of causing the destruction of anthocyanins and a consideration of some of its properties. The anthocyanase activity of several varieties of sweet cherries and of several types of berries was determined at various stages of maturity. Anthocyanase is believed to participate in the early stages of scald in red sour cherries through destruction of anthocyanin pigments. Sour cherry anthocyanase was prepared from homogenates of fresh fruit and partially purified from press juice by ammonium sulfate precipitation. The enzyme has limited solubility in water and exhibits maximum activity at pH 5.7 to 6.0. The enzymatic activity of a homogenate of fresh cherries was nearly doubled by the addition of catechol. Purified enzyme preparations were nearly inactive unless catechol was added. The optimum concentration of catechol was 0.01M. The anthocyanase of sour cherries requires the participation of oxygen for activity and was inhibited by thiourea. Sour cherry anthocyanase is quite similar in its properties to Coleus cyanin oxidase, and is dissimilar to fungal anthocyanase. The presence of anthocyanase has also been demonstrated in sweet cherries, black raspberries, blackberries and blueberries. The amount of enzyme activity in these fruits at several stages of maturity has been studied. (See page 47.)

Starch technology — *Use of pregelatinized starches*

Pregelatinized starches for the food processor. Leonard M. Waldt.

A pregelatinized starch is produced by cooking and drying the starch dispersion on heated rolls or drums. This process involves feeding a starch slurry (after completion of processing, refining, and blending with other starches, sugars, etc.) on the outer surface of a steam-heated revolving drum. The rate of rotation of the drum is set so that the material is dried and scraped off by a doctor blade when the drum reaches a certain position. The operation can be performed on single or double drums, with the latter providing greater capacity. This pre-cooking process swells the starch granules and thus conditions them to thicken and gelatinize in cold liquids, without need for subsequent heating. Thus, the starch manufacturer is doing the actual starch cooking operation in his own plant. By this method, gelatinization time, gel texture, stability and composition can be engineered into the starch according to the requirements of the food manufacturer's equipment and the food product involved. Product uniformity from item to item and batch to batch is assured and the user is relieved of the costly cook-up and gelatinization control operations necessary with ordinary starches. Unfortunately, there is a dearth of literature (except for patent claims) on pregelatinized starch use and application. This paper outlines some of the advances made in the starch technology field in recent years and provides suggestions on how a food processor can take advantage of the properties of precooked starches through proper examination, control, and intelligent application. (See page 50.)

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Identification of pink pigment — *Canned Bartlett pears*

Pink discoloration in canned Bartlett pears. B. S. Luh, S. J. Leonard, and D. S. Patel.

In this article the effects of growing area, soil types, and processing conditions on pink color development in canned Bartlett pears are reported. A method for quantitatively determining the pink-color precursor is presented. The pink pigment in the canned product was investigated by chromatographic methods. Growing area and soil types were found to be related to this problem. Pears from certain growing areas had low pH, high acidity, and high tannin content. These pears were found to develop pink color after canning, especially when excessive heating and delayed cooling processes were used. The pink pigment in canned pears was shown to be identical in R_f value to that of cyanidin. (See page 53.)

Freezing technology — *Corn starch and starch derivatives*

Characteristics of corn starch and starch derivatives as affected by freezing, storage and thawing. I. Simple systems. James J. Albrecht, A. I. Nelson, and M. P. Steinberg.

When thawed after some time in frozen storage, most food products thickened with starch exhibit a curdled appearance and liquid separation. The original smoothness is not completely regained even in foods reheated before serving. Such texture changes have been commonly grouped under the term "retrogradation." The over-all objective of this investigation was to determine the effects of rate of freezing, storage tempertaure, shearing of granule systems, and heat treatment prior to freezing on the freeze-thaw stability of the simple combination of thickening agent and water. Three starch products were chosen to serve as a representative group of thickening agents: (1) a standard or natural corn starch, (2) a pregelatinized cross-linked waxy maize starch, and (3) a starch phosphate. Effects of various processing variables on the freeze-thaw stability of starch slurries were investigated. Other variables were processing of the slurry, rate of freezing, storage temperature, thawing and post-thaw treatment. The susceptibility of the starch to enzyme action generally decreased with an increase in starch retrogradation as indicated by sponge formation, syneresis, and lumpiness. Retrogradation was essentially eliminated from frozen Reg. PFP starch slurries which had not been heated to the critical gelatinization temperature. It was shown that the enzyme susceptibility of slurries of HR W-13 starch and starch phosphate did not significantly change as a result of freezing and thawing. Similarly, preheating of such slurries to temperatures as high as 185° F. had no noticeable effect on freeze-thaw stability. Retrogradation was found to take place at the most rapid rate during the 24-hour period after the starch slurries had been placed in frozen storage, and continued to take place at a much slower rate during subsequent storage. Freezing starch slurries instantaneously by direct immersion in liquid nitrogen made it possible to eliminate

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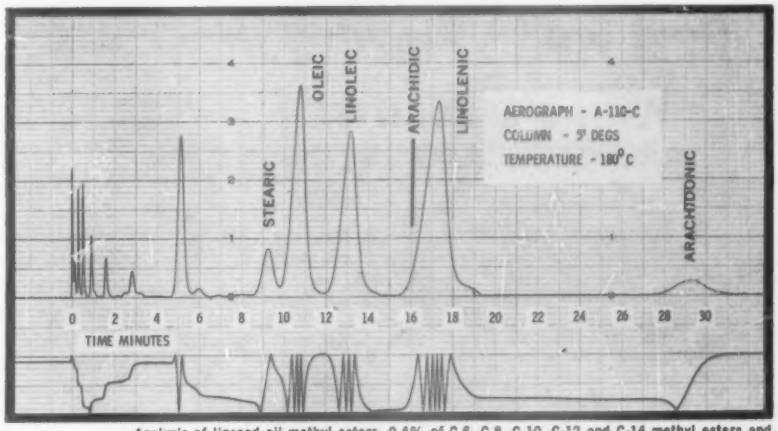

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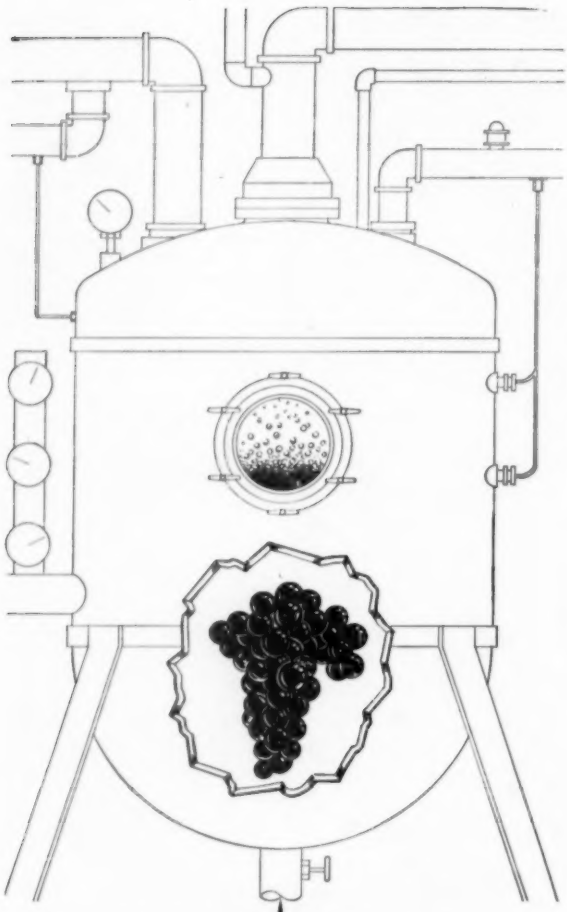
sponge formation from samples of pregelatinized regular corn starch and the curdled appearance from waxy maize slurries. After storage at 0° F. for one week, samples frozen by this method gave no indication of retrogradation. (See page 57.)

Freezing technology *White sauces*

Characteristics of corn starch and starch derivatives as affected by freezing, storage and thawing. II. White sauces. James J. Albrecht, A. I. Nelson, and M. P. Steinberg.

Objective of this research was to produce a typical white sauce system stable to freezing, frozen storage, and subsequent thawing at room temperature. Of special significance was the use of high-pressure homogenization techniques and instantaneous freezing of white sauce systems using liquid nitrogen. Other treatments involved gelatinization and storage temperature effects. Replicated samples were organoleptically evaluated. To determine the applicability of the findings on freeze-thaw stability of starch-water slurries, these investigators employed standard white sauces prepared with regular corn starch, pregelatinized, cross-linked waxy maize starch and starch phosphate. For the control white sauce they used all purpose flour as the thickening agent. Treatments included severe homogenization and freezing in liquid nitrogen. Using a six-member taste panel, samples were evaluated for smoothness, liquid separation, mouth feel, flavor, and general acceptability. Taste panel and enzyme susceptibility data were analyzed using a single degree of freedom statistical analysis of variance. Storage was found significant at the 1% level in all cases with respect to some storage versus no storage. Freezing in liquid nitrogen was not statistically significant. Thus, there was no benefit to be derived by extremely rapid freezing of white sauces—in direct contrast to results obtained with starch-water systems. On the other hand, severe homogenization of white sauces prior to freezing significantly increased the freeze-thaw stability of these sauces; this result was again in direct contrast to results obtained with starch-water systems. However, these samples were not subjected to long storage periods, which might counteract the favorable effects of severe homogenization. The enzyme susceptibility test was found to be unsatisfactory as an index of freeze-thaw stability of standard white sauce in contrast to the simple starch-water system. Some techniques which greatly improved the stability of simple starch-water systems had little such beneficial effect on white sauces. Other processing treatments gave the opposite results. It was concluded (1) that a complex relation exists between the thickener and other ingredients in a white sauce and (2) the thickening agent itself cannot be solely responsible for the curdled appearance of frozen white sauces. Based on results of investigations concerning both white sauces and starch-water systems, thickening agents were rated in decreasing order of freeze-thaw stability, as follows: (1) starch phosphate, (2) ungelatinized regular corn starch (this technique is limited to products in which solids need not be suspended during freezing and storage and to products which are heated to near the boiling point before consumption), (3) pregelatinized, cross-linked waxy maize starch, (4) all-purpose flour, and (5) regular corn starch (which is gelatinized prior to freezing as part of the sauce formulation process). (See page 64.)



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(Manuscript received May 21, 1959)

THE FOOD INDUSTRY is constantly striving to improve the efficiency of its operations and the quality of its products. With regard to potatoes, one operation that has been investigated with a view to improvement is the preparation of the raw product; specifically, peeling. Many types of peeling have been used. Lye has long been used, as a patent issued to Dunkley *(2)* in 1914 for such a procedure, indicates. In 1943, Mazzola *(8)* proposed a method of peeling wherein a very high concentration of lye and high temperature for short durations of time are used.

Wright *(9)* who ran tests on peeling potatoes by the abrasive method, showed peel losses from 14 to 31%, depending on the variety and size of the potato. Harrington, Mayer, Olson, Mullins and Potter *(4)*, studying lye peeling, found that the optimum lye concentration for peeling French fries was 15 to 20%. The U. S. Department of Agriculture has issued a report covering the cost of peeling potatoes by lye and abrasive methods *(3)*. In 1953, 39% of the potatoes processed were peeled by lye, whereas, in 1955, nearly 54% were so peeled. The U.S.D.A. survey showed that peel loss from abrasive peeling was 24.9%, from lye 22.4%, and from steam 18.6%. It was found to be cheaper to peel with lye, if the production rate was over 425 bags per week, and the cost of the raw material was $1.50 per 100 lbs.

Whether a mechanical lye peeler or a steam peeler is used—each has its limitations. However, a comparatively new method, pre-coating products with hot caustic solution, and then subjecting them to atmospheric steam under pressure, has been shown to offer greater flexibility than other techniques, and better process control. Hickey and Kilburn developed this procedure in 1948. They were issued patents (U. S. 2,781,070 and U. S. 2,847,334) in 1957 and 1958 *(6, 7)*. This paper will present the advantages of such a system—comparing its labor saving, yield, and flexibility of application against the same factors when steam or lye alone is used. Since processors are becoming more and more cognizant of the costs of operation and yield, the concepts introduced here should be of much interest. Also studied were the holding times in lye and steam in order to determine peel loss and peeling efficiency.

* Presented at the Nineteenth Annual Meeting of the Institute of Food Technologists, Philadelphia, Pennsylvania, May 19, 1959.

EXPERIMENTAL PROCEDURE

Idaho Russets (field run No. 1) were used for the peeling tests, which were conducted at the Rogers Brothers' plant in Idaho. The potatoes were counted and weighed prior to the peeling tests, and then were subjected to lye immersion and the commercial lye applicator; next they were transferred to a continuous pressure steamer and washed in a rotary reel washer, after which they were placed on an inspection belt. The potatoes were then counted and re-weighed to determine the per cent peel loss. Fifty potatoes (medium size) were used for each test unless the potatoes were quite small, in which case 100 were used for the run. The results of the peeling efficiency tests were determined by visual observation. The designations were *poor, fair, good,* and *excellent*. The per cent peel loss reported does not include trim loss. Trim loss varies, depending on the defects noted in the potato. The flow sheet presented in Figure 1 delineates the operation of peeling.

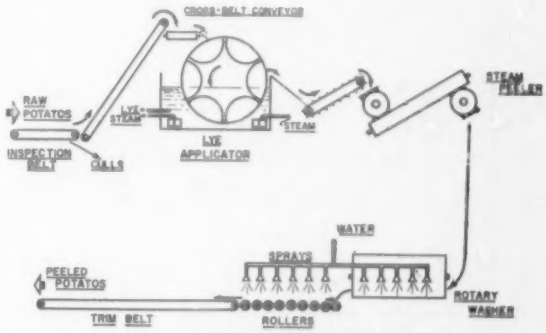

Figure 1. Lye-steam potato peeling.

Surface area data were collected by dissecting the potatoes in quadrants and tracing the outline on graph paper. These tracings were cut out and weighed on an analytical balance. Then, knowing the weight of 1 square inch of paper, the surface area in square inches of the potato was computed.

RESULTS AND DISCUSSION

In determining peel loss, the size of the potato must be considered. A large potato will have less loss by weight than a small one, due to increased surface area. The data presented in Figure 2 relates the weights of potatoes to the corresponding surface areas. Each potato will vary in weight and surface area, but in general as the weight increases, so does the surface area. Based on this information, different sized potatoes were weighed and peeled; their surface areas were taken from Figure 2.

Correlation of peel loss and surface area was made. The results are to be found in Figure 3. Obviously, the curve is asymptotic at both ends, since an increase in surface area would not result in 0% peel loss.

A study was made of peeling loss, using 5 and 10% lye plus steam as well as a test using 5% lye with a wetting agent added. Various immersion times in lye and exposure times in steam were used to study the peeling loss and the peeling efficiency. Since defects and rot were not removed from the potatoes in any run, trim loss is not included.

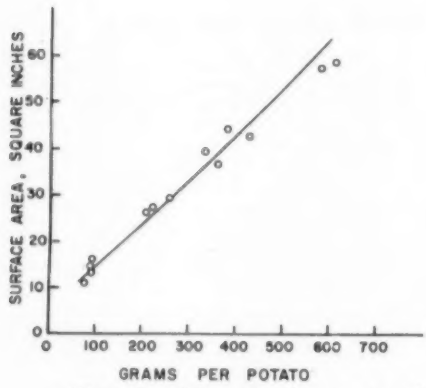

Figure 2. Relation of surface area to weight.

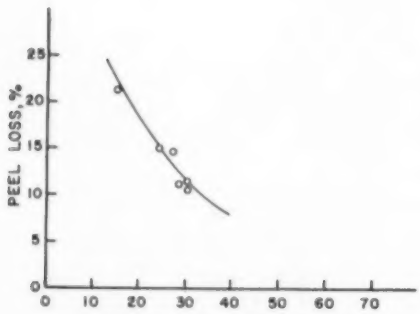

Figure 3. Effect of surface area on peel loss.

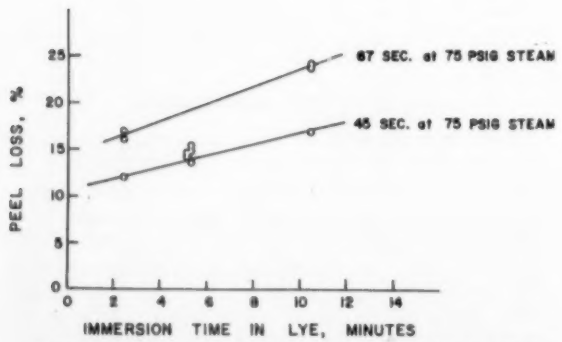

Figure 4. The effect of immersion time on peel loss in 5% lye @ 175° F. followed by two holding times in steam.

Increasing immersion time in lye and exposure in steam increased the peel loss using 5% lye (Figure 4). Optimum peeling conditions appear to be 5½ minutes in lye and 45 seconds at 75 p.s.i.g. steam with a peel loss of 14.6%. Decreasing the lye time and increasing the exposure to steam resulted in a peel loss of 16.8%.

It is interesting that the use of a wetting agent minimized the peel loss at various immersion times in lye. Comparing Figure 5 to Figure 4, there is less

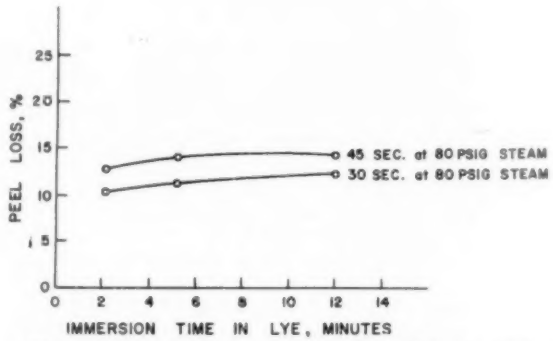

Figure 5. The effect of immersion time on peel loss in 5% lye @ 190° F. plus 0.1% wetting agent followed by two holding times in steam.

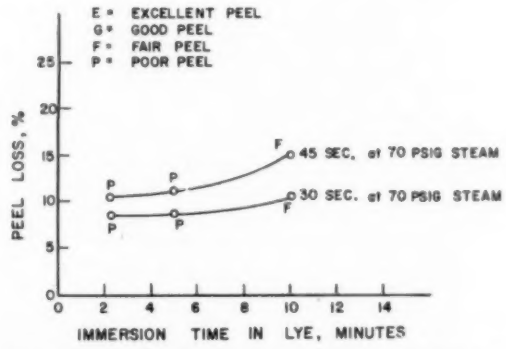

Figure 6. The effect of immersion time on peel loss in 10% lye @ 180° F. followed by two holding times in steam.

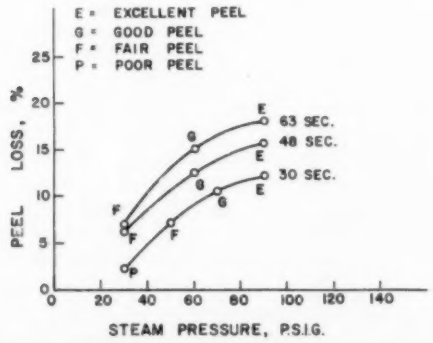

Figure 7. The influence of steam pressure on peel loss. The potatoes were immersed 5 minutes in 5% lye @ 180° F. followed by three different steam holding times.

peel loss at 45 seconds in 80 p.s.i.g. steam with 5% lye using a wetting agent than without the wetting agent. The holding time in lye has no appreciable influence on peel loss (Figure 5).

The use of 10% lye increased the peel loss when a 10-minute immersion time was employed (Figure 6). There was a greater peel loss at 45 seconds in 70 p.s.i.g. steam, than at 30 seconds when the potatoes were immersed for 10 minutes in lye. The peeling efficiency was better at longer lye and steam exposure times. Higher concentrations of lye resulted in more peel loss, if the peeling efficiency was maintained.

Runs were made varying the steam pressure to determine peel loss and peeling efficiency (Figure 7). The potatoes were held 5 minutes in 5% lye and exposed to different steam pressures and exposure times. Increasing steam pressure and exposure increased the peel loss; maximum peeling efficiency was found to be 30 seconds at 90 p.s.i.g. with a peel loss of 12.3%.

The effect of lye temperature on peel loss for exposures of 5 and 10 minutes is shown in Figure 8. The

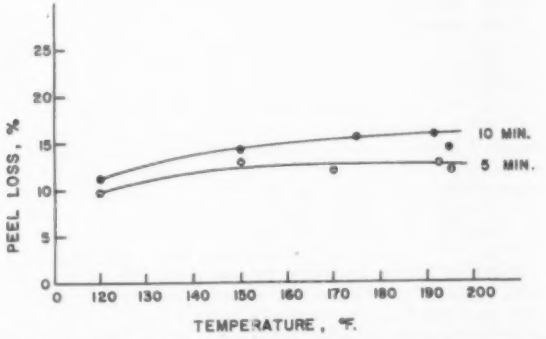

Figure 8. The effect of lye temperatures on peel loss at two immersion times in 5% lye. The potatoes were processed 45 seconds @ 75 p.s.i.g. steam after lye treatment.

curves show a flattening in the region of the gelatinization temperature of potato starch. The interpretation of this is that gelationization and rupture of cells in the parenchyma region at higher temperature hinders penetration of caustic, which limits cell lysis and consequently peel loss on washing.

Peeling other food products. The application of steam-chemical peeling of apples has shown much promise in the laboratory. The peeling removes all the skin, even around the stem of the apple by this method. Various sizes and varieties of onions have been peeled, and a definite number of layers of skin can be removed, depending on the hold time in lye and steam. Sweet potatoes, carrots, beets, as well as wheat, corn, nuts, tomatoes and pimentos have been peeled. Commercial application of some of these products has not been completely developed at this time.

Cost analyses. Based on commercial data, a comparison was made of the various methods of peeling potatoes. The cost figures were based on the labor, lye, and product yield. This information is presented in Table 1, showing the difference in cost per ton of peeled potatoes.

Table 1 shows that it would require $5.50/ton more to peel using only lye than it would by the combination lye-steam method, and $1.60/ton more to peel by straight steam rather than lye-steam. The labor costs were based on a survey *(1)*, as well as on information from Government publications on chemical and labor costs *(3)*.

TABLE 1

Cost data on peeling potatoes

Method	Per cent peel loss	Dollars/ton cost difference
Lye	22.4	5.50
Steam	18.6	1.60
Lye and steam	21.0	0

Table 2 presents the cost and usage of lye required for the two methods using lye and the combination of lye plus steam.

The reason that the consumption of lye is higher for straight lye peeling is due perhaps to the fact that the potatoes are immersed in lye for a longer period. The potatoes tend to absorb more lye as well as more carryover than when the lye-steam peeling method is used.

TABLE 2

Costs and usage of lye

Method	Lb. lye/ton potatoes	Cost lye/ton potatoes
Lye (15%)	24	$1.20
Lye + steam (5%)	2.4	.12

SUMMARY

Correlation of surface area to peel loss was studied, using Idaho potatoes., As surface areas increase, peel loss is decreased. Five per cent lye followed by 45 seconds at 75 p.s.i.g. steam resulted in good peeling, the peel loss being 14.6%. Addition of a wetting agent to 5% lye, followed by steam, produced good results with high yield. Cost analyses on three peeling methods indicated lye plus steam is the most economical method of peeling.

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The Quality of Grain-Finished and Grass-Finished Beef as Affected by Ripening

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FEED MANAGEMENT and ripening are two of the many interacting factors affecting the quality of beef as judged by the producer, packer, and consumer. It is recognized that ripening up to a certain point improves the eating qualities of beef, but the effects of specific feeding regimes do not seem quite so clearly defined. Thinking differs as to the merits of grass-finishing versus grain-finishing in preparing beef for market. The popular opinion seems to be that grain-fed beef is superior to grass-fed.

One of the earliest comparisons of the quality of grain-finished and grass-finished beef was made by Black, Warner, and Wilson *(3)* in 1931. They reported no difference between the two types other than in tenderness. Beef fed a supplement of corn and cottonseed meal was determined to be slightly more tender than beef fed only on pasture. Both taste panel scores and shearing strength values were used as criteria of tenderness. In 1940 Black, Hiner, Burk, Alexander, and Wilson *(2)* found no important differences either in tenderness or in other palatability factors between beef from animals fed exclusively on grass and those on grass supplemented with concentrates. On the other hand, Bull, Snapp, and Rusk *(4)* reported inferior eating qualities for grass-fed beef because of lower finish. Likewise, Wanderstock and Miller *(10)* found beef from animals fattened on pasture alone to have poorer eating qualities than that from animals fed supplements, or fed in dry lot. However, all of the beef was scored as acceptable. The superiority of the supplement-fed and dry-lot beef was attributed largely to higher finish. In 1953, Hunt, Kincaid, and Carter *(6)* concluded that there was no difference in the quality of grain-fed and grass-fed beef provided both types were equally fat.

Only limited work has been done to test the effects of ripening on beef from animals finished on different feeds. Barbella, Tannor, Hankins, and Hunt *(1)* found little or no difference in flavor and aroma of meat from grain-fattened and grass-fattened steers after 15.7 and 50 days of ripening. Chemical tests indicated that the sulfhydryl content of the grass-fattened beef was higher than that of the grain-fattened at 15.7 days, but the difference was not significant at 50 days of ripening.

The purpose of the work reported here was to test the effects of limited and extensive ripening on the palatability of beef from grain-finished and grass-finished steers. Other conditions which might affect palatability factors were controlled as far as possible.

EXPERIMENTAL

Experimental design. Meat for this study came from 8 pairs of steers, tested over a period of 2 years. Both dry-heat and moist-heat cooking methods were employed. Roasts for dry-heat cooking were cut from the *longissimus dorsi* muscle, in the loin and posterior-rib area, and roasts for braising were cut from the *semimembranosus* muscle of the round. Both types of cooked roasts were tested by sensory-difference measurements and shearing at 2, 7, 21, and 42 days of ripening.

Feed management. Of the 8 pairs of steers tested, 5 were Hereford and 3 were Angus. Pertinent data on these animals are tabulated in Table 1. The animals of each pair were matched as closely as possible as to age and genetic background. The grain-finished steers were full fed a mixture of corn and cottonseed meal in dry lot an average of approximately 5 months prior to slaughter. Most of the animals were on pasture plus some grain before full feeding began. The grass-finished steers were on pasture their entire lives except during times of inclement weather when a limited amount of dry roughage or silage with cottonseed meal was fed. For the most part the pasture was orchard grass and Ladino clover.

Ripening. After slaughter, the carcasses were chilled, then aged at 33° F ± 3° (humidity approximately 85%). Samples were removed from one side of a carcass for the first 2 test periods, and from the other side for the last 2 tests. The meat was aged as sides until the 21st day, samples being removed as needed. On the 21st day the remaining sections of the loin and round were removed and covered with wax, to be held in the cooler until the 42nd-day tests.

Cooking. All roasts were boneless cuts. Cooking was done in a revolving-hearth, Despatch oven at 300° F., the temperature recommended by the National Cooperative Meat Investigations *(5)*, for experimental roasting of beef.

The loin roasts were cut 4 inches thick. Those from the grain-finished animals averaged 2.2 lb., and from the grass-finished, 1.8 lb. They were cooked uncovered to an internal temperature of 158° F.

The round roasts were 2 inches thick. The average weight for the grain-finished was 2.7 lb., and for the grass-finished, 2.5 lb. They were first browned 7[c] minutes on each side in a heavy, aluminum skillet at 325° F. surface temperature, then covered and cooked in the oven without added liquid to an internal temperature of 208° F. Necessary weights were taken before and after cooking in order to determine cooking losses.

Shears. Three, 1-inch cores were taken from the same location in each cooked roast and cooled to room temperature for shearing. A Warner-Bratzler shearing machine was used. Each core was sheared twice, giving 6 measurements for shearing-strength averages.

Sensory-difference tests. A trained panel of 5 judges[d] scored the meat for tenderness, flavor of lean, flavor of fat, and juiciness. The panel was trained by scoring paired roasts. One roast of each pair had been frozen unripened and the other frozen after ripening for 14 to 21 days. Ability to consistently dif-

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[b] Published with the approval of the Director of the Tennessee Agricultural Experiment Station, Knoxville.

[c] Five minutes on each side for the 42-day ripening period.

[d] Four judges for one pair.

TABLE 1

Data on steers used for feeding and ripening tests

Pair	Breed	Type of feed	Slaughter data			Time full-fed grain
			Age	Weight	Grade[1]	
			mo.	*lbs.*	*U.S.D.A.*	*mo.*
A	Hereford	Grain	24	1070	High Good	8
		Grass	23	870	High Standard	....
B	Angus	Grain	16–18	990	High Good	3.5
		Grass	16–18	965	Average Good	....
C	Hereford	Grain	18	985	High Good	6
		Grass	23	916	Average Good	....
D	Hereford	Grain	23	1065	High Good	6.5
		Grass	23	980	Average Good	....
E	Hereford	Grain	18	1020	Low Choice	2
		Grass	20	864	Average Good	....
G	Hereford	Grain	23	1050	Low Choice	5
		Grass	23	930	Average Good	....
H	Angus	Grain	29	820	Low Choice	4
		Grass	25	728	Low Good	....
I	Angus	Grain	20	.....	High Good	4
		Grass	20	.....	Low Good	....
Average		Grain	21.5	1000	High Good +	4.9
		Grass	21.8	893	Low Good +	....

[1] All carcasses were graded by an official U.S.D.A. Grader.

ferentiate the ripened from the unripened meat was the criterion applied in selecting panel members. As the study progressed replacement judges practiced scoring meat actually under test.

Scoring was done on a 9-point scale ranging from 9 to 1, *excellent* to *very poor*. For scoring the lean, each judge received a slice cut from the same relative position of each roast for every pair of animals. For scoring flavor of fat, a portion of the external fat trimmed from the roast before slicing was presented to each judge. Coded samples on individual plates were scored immediately after carving. Four samples were scored at one sitting, one from the loin roast and one from the round roast of each type of beef.

Statistical methods. The data were tested by analysis of variance. A split-plot design was used, with feeds as main plot and ripening periods and muscles as subplots. The Studentized Range as described by Snedecor *(8)* was used to test significance. Missing-plot data were calculated for one pair of steers, one muscle, and one aging period. Simple correlation coefficients were used to determine the relationship existing between panel tenderness scores and mechanical shear values.

RESULTS

Tenderness. Data for tenderness as measured by sensory panel and by shear value are shown in Table 2. Both criteria indicate that the grain-finished beef was more tender than the grass-finished. This difference was significant as measured by taste panel (Table 6). While the shear values for the grain-finished beef were consistently lower than for grass-finished, the difference was not significant.

Ripening caused a highly significant (P.001) improvement in the tenderness of both grain- and grass-finished beef whether measured by panel or shear value. Most of the increase in tenderness occurred during the first 21 days of ripening. Beyond this point, panel scores and shear values for the loin roasts tended to level off. The round roasts continued to increase in tenderness but at a slower rate, up to 42 days of ripening. Although the grain-finished was the more tender of the 2 types, it should be pointed out that there was relatively more improvement in the tenderness of the grass-finished beef, so that after 6 weeks of ripening differences in tenderness between the 2 types were less marked than during the earlier periods.

A comparison of all panel scores for tenderness with shearing strength values gave a correlation of −0.41 which was highly significant. Likewise, the correlation of panel scores with shear values of loin roasts for all aging periods combined was highly significant. However, correlation for single aging periods tended not to be significant.

Flavor of lean. Data for flavor of lean, flavor of fat, and juiciness are shown in Table 3. The lean of grain-finished beef scored significantly higher (P.001) in flavor than that of grass-finished beef (Table 6). The difference between the 2 types was more noticeable in the loin roasts where the average scores differed by 1.1 points, than in the round roasts where the difference was 0.7 point.

Ripening afforded little or no improvement in the flavor of the lean of grass-finished beef, but tended to improve the flavor of the grain-finished lean up to the 21st day. Over-all, the flavor of lean scores decreased significantly between the 21st and 42nd day of ripening, the decreases being more marked for the grain-finished.

Flavor of fat. As indicated by the data in Table 3, the greatest sensory difference between the 2 types of beef was observed in the flavor of the fat. Differences attributed to feed were highly significant (P.001) (Table 6), the fat of the grain-finished beef being much more acceptable to the panel (Table 3). Ripening for 21 or 42 days caused significant decreases in the scores for fat flavor of either type of beef.

In an effort to account for the differences in fat flavor between the 2 types of beef, and for the impairment due to ripening, external fat samples from the last 3 pairs of steers were analyzed for per cent free fatty acid and peroxide values. Both heated and unheated samples were analyzed to determine if the

TABLE 2

Tenderness scores and shearing strength measurements of grain-finished and grass-finished beef after ripening

Number of days of ripening	Grain-finished		Grass-finished	
	Panel score	Shear in lbs.	Panel score	Shear in lbs.
Longissimus dorsi				
2	6.6	19.8	5.7	21.7
7	7.7	14.6	6.9	17.1
21	8.2	13.3	7.8	15.6
42	8.4	14.0	8.0	14.2
	Correlation = −0.52**		Correlation = −0.52**	
Semimembranosus				
2	6.8	20.3	5.8	24.7
7	6.4	18.0	5.8	20.2
21	7.4	14.7	6.8	16.4
42	7.6	11.4	7.3	12.4
	Correlation = −0.35		Correlation = −0.37*	

* Significant at P.05.
** Significant at P.01.

TABLE 3

Flavor and juiciness scores[1] for loin and round roasts from grain-finished and grass-finished beef after ripening

Number of days of ripening	Flavor of lean		Flavor of fat		Juiciness	
	grn.	grs.	grn.	grs.	grn.	grs.
Longissimus dorsi						
2	7.4	6.6	7.7	6.1	8.3	7.6
7	7.7	6.5	7.4	5.6	8.0	7.8
21	7.9	6.6	6.5	4.7	8.2	7.7
42	7.3	6.4	6.4	4.7	7.9	7.5
Av.	7.6	6.5	7.0	5.3	8.1	7.6
Semimembranosus						
2	7.5	6.8	7.9	6.1	5.8	5.0
7	7.6	7.0	7.9	6.1	5.6	5.1
21	7.8	6.9	7.1	5.7	5.5	5.0
42	7.1	6.5	6.9	5.2	5.6	5.2
Av.	7.5	6.8	7.4	5.8	5.6	5.1

[1] Each figure an average of 8 tests.

flavor deterioration was due to the effect of ripening per se, or whether the heat of roasting imposed flavor deterioration on the aged fat. The preparation of the fat samples has been described *(9)*. Averages of these data are shown in Table 4. This limited work yielded no indication that the grass-finished fat had any greater tendency to either oxidize or hydrolyze than did the grain-finished fat. Aging for 42 days caused an increase in acid development in both types. Thus it seems possible that hydrolysis may account in part for the flavor deterioration of the fat during ripening. It can only be surmised that some fat-soluble substance(s) absorbed by the fatty tissue may have contributed to the less desirable flavor of the fat of beef finished on pasture.

Juiciness. Grain-finished beef was scored as significantly (P.001) more juicy than the grass-finished beef (Tables 3 and 6). This was true for both the medium-done loin roasts and the well-done round roasts, even though the round roasts were significantly less juicy than the loin roasts. Since "it is generally conceded that the presence of fat around and within the muscle increases the juiciness of the cooked meat" *(7)*, this difference was to be expected, because the grain-finished steers averaged about two-thirds of a grade higher than the grass-finished steers. Juiciness was neither improved nor impaired by ripening.

Cooking losses. Over-all differences in drip losses, evaporation losses, and total cooking losses due to feed were not significant (Tables 5 and 6). However, the average drip loss from the loin roasts of the grain-finished animals was higher than that from the grass-finished animals. The higher fat content of the grain-finished roasts probably accounted for this difference.

Ripening produced a progressive increase in drip losses and in total losses that was highly significant (P.001). This increase was much more evident in the drip from the loin roasts than from the round roasts of both types of beef. Evaporation losses were not significantly affected by ripening.

DISCUSSION

In this study both kinds of beef were scored at the same time making comparisons between the two inevitable. Under these conditions, the grain-finished beef scored significantly superior to the grass-finished beef in flavor of lean, tenderness, flavor of fat, and juiciness. However, when the scores for both loin and round roasts were combined, the average differences between the two types were 0.9, 0.6, 1.65, and 0.5 points respectively. On the basis of the 9-point scale used in this study, it might be questioned whether these differences are great enough to consider the grass-finished beef inferior from a consumer standpoint, especially in flavor of lean, tenderness, and juiciness. On the other hand, the more decided difference in flavor of fat would perhaps be of importance to consumers. The question also arises as to whether the differences between the grain-finished and grass-finished beef would have been as great or greater had each sample been presented to the panel as a single stimulus and at different times.

TABLE 4

Peroxide numbers and per cent free acid of external fat[1] from grain-finished and grass-finished beef after ripening

Number of days of ripening	Peroxide number		Free acid (Per cent as oleic)	
	grn.	grs.	grn.	grs.
Heated samples				
2	0.51	0.44	0.26	0.25
7	1.82	1.82	0.53	0.45
21	0.82	0.59	1.79	2.97
42	4.26	4.01	10.74	11.99
Unheated samples				
2	0.07	0.25	0.03	0.03
7	0.12	0.21	0.06	0.06
21	0.26	0.50	1.43	0.53
42	1.06	0.67	9.75	11.05

[1] Each figure is the average of 3 determinations.

TABLE 5

Cooking losses[1] of loin and round roasts from grain-finished and grass-finished beef after ripening

Number of days of ripening	Evaporation loss, per cent		Drip loss, per cent		Total loss, per cent	
	grn.	grs.	grn.	grs.	grn.	grs.
Longissimus dorsi						
2	11.9	11.9	6.4	3.7	18.3	15.6
7	11.9	12.0	8.2	4.5	20.1	16.5
21	11.7	12.2	10.1	7.3	21.8	19.5
42	11.9	13.1	12.2	8.8	24.1	21.9
Av.	11.8	12.3	9.2	6.1	21.1	18.4
Semimembranosus						
2	11.7	11.5	28.4	29.6	40.1	41.1
7	11.4	11.9	29.0	29.8	40.4	41.7
21	12.1	12.8	29.7	30.7	41.8	43.5
42	10.0	10.3	31.1	31.4	41.1	41.7
Av.	11.3	11.6	29.6	30.4	40.8	42.0

[1] Each figure is the average of 8 determinations.

Two breeds, Hereford and Angus, were used in this study and there was considerable variation in the length of time on full grain feed. The data indicate, that for the palatability factors tested, no differences were associated with either breed or length of time on feed.

Ripening affected the flavor of fat, juiciness and cooking losses of the two types in a somewhat parallel manner, but the flavor of lean of the grain-finished beef showed a trend toward improvement not obtained with the grass-finished beef. The grass-finished beef showed more relative improvement in tenderness during ripening than did the grain-finished beef. With this panel and with the grade of meat tested, ripening beyond 21 days seemed to produce diminishing returns. The slight increase in tenderness obtained after 21 days, tended to be offset by impairment in the flavor of the lean and fat.

SUMMARY

The effects of 2, 7, 21, and 42 days of ripening on the palatability of grain-finished and grass-finished beef were studied. Medium-done loin roasts cooked by dry heat, and well-done round roasts cooked by moist heat were tested by a sensory-difference panel for tenderness, flavor of lean, flavor of fat, and juiciness.

TABLE 6

Mean squares for palatability scores and per cent cooking losses

Source	df	Tenderness		Flavor		Juiciness	Cooking losses		
		Warner-Bratzler shear	Sensory panel scores	Lean	Fat		Per cent drip	Per cent evaporation	Per cent total
Replications (Pairs)	7	29.60	0.78	0.56	0.80	0.42	14.01	3.09	18.09
Feeds	1	129.81	13.52*	24.50***	92.48***	8.20***	41.90	5.59	16.89
Error (Main plot) (Reps x Feeds)	7	33.88	2.09	0.34	1.05	0.11	16.52	3.95	20.48
Ripening periods	3	439.23***	18.17***	1.64***	10.31***	0.11	91.68***	4.17	79.92***
Muscles	1	32.30	15.40***	0.28	6.84***	206.04***	15831.10***	12.37	14958.01***
Ripening periods x Muscles	3	42.26**	2.52***	0.08	0.54	0.19	18.17**	11.63*	41.56***
Ripening periods x Feeds	3	9.75	0.59	0.24	0.03	0.19	1.37	1.12	1.06
Feeds x Muscles	1	3.09	0.01	1.12*	0.00	0.02	125.83***	0.10	118.66***
Feeds x Ripening periods x Muscles	3	3.61	0.07	0.07	0.12	0.04	0.20	0.63	1.35
Error (Subplots)	96	9.55	0.39	0.23	0.35	0.19	3.40	3.15	3.91

* Denotes significance at P.05. ** Denotes significance at P.01. *** Denotes significance at P.001.

Objective estimates of tenderness were made with a Warner-Bratzler mechanical shear. Cooking losses were determined.

The grain-finished beef was scored significantly higher than the grass-finished beef for tenderness, flavor of lean, flavor of fat, and juiciness. Tenderness differences due to feeding regimes were not significant when measured by shear machine. There were no significant differences in cooking losses attributable to feed.

Both types of beef exhibited highly significant increases in tenderness due to ripening, but relatively more improvement was shown by the grass-finished beef.

The flavor of lean of the grain-finished beef tended to improve up to 21 days of ripening, but the flavor of lean of the grass-finished beef showed little or no improvement during ripening. After 21 days, the scores for flavor of lean decreased significantly.

Flavor of fat of both types of beef was significantly impaired with 21 and 42 days of ripening. Some evidence was obtained that free fatty acid developed between 21 and 42 days of ripening.

Juiciness was not significantly affected by ripening.

There were highly significant increases in drip losses and total cooking losses due to ripening, but evaporation losses were unaffected.

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Improving the Stability and Acceptability of Precooked Freeze-Dried Ham[a, b, c]

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NUMEROUS PUBLICATIONS *(2, 3, 5, 9, 11)* have reported that freeze-drying of meat produces a product far superior to that which can be obtained by conventional high-temperature vacuum methods. Although freeze-dried meat initially possesses a number of ideal quality characteristics, deterioration does occur during subsequent storage.

In their comprehensive review on freeze-drying, Harper and Tappel *(5)* discuss and describe the adverse changes occurring in freeze-dried beef during storage, while Sharp *(6, 7)* has reported on the nonenzymic degradation of freeze-dried pork.

Studies have been cited *(5)* which indicate that freeze-dried beef has a suitable storage stability for six months at 100° F. and freeze-dried pork chops exhibited good storage stability for one year both at 70° F. and 100° F. With cured meats, however, Wodicka *(11)* has stated that the freeze-dried samples became rancid after a few weeks of storage, although the initial quality was good. It was hypothesized that the curing ingredients of commercially cured hams were responsible for these changes. Accordingly, experiments were designed in which curing methods, alteration and substitution of curing ingredients, time and temperature of curing, and precooking conditions were modified in an attempt to increase the storage stability. Results of these investigations and those obtained by the use of various stabilizers and of a long term storage study are reported herein.

EXPERIMENTAL

Curing methods. Hams were injected with a sterile 75° salometer pickle equivalent to 10% of their green weight by artery, spray and stitch pumping. The pickle consisted of salt and cane sugar in the ratio of 8:3, with sodium nitrate and sodium nitrite being added at levels of 0.15% and 0.09%, respectively. Sodium isoascorbate[d] was added to the pickle at the rate of 2.62 g. per gallon immediately prior to pumping. For cover pickle, the above solution was diluted to 65° salometer. Hams were held in cure for 6 days at 38° F.

Alteration and substitution of curing ingredients. A number of 75° salometer pickles were tested and in each the salt and sugar were held constant at a ratio of 8:3, while the amounts of sodium nitrate and sodium nitrite were varied. Nitrate and nitrite were added to pickles at 4 different levels: 0.065, 0.13, 0.195 and 0.26% of total pickle, either as the sole color fixative agent or in various combinations with one another.

In later experiments, the pumping pickle was diluted from 75° salometer to 60°, 40° and 20° salometer, while monosodium glutamate was added at levels of 0.05%, 0.1% and 0.15%, respectively. In these brines, sugar was completely replaced with Sucaryl[e] (sodium cyclamate) at the rate of 1 part Sucaryl equals 32 parts sugar. Nitrate and nitrite levels were 0.15% and 0.09%, respectively. Hams were artery pumped with the above pickles and held for 6 days in a cover brine of the same strength as that with which they were pumped.

Hams were also cured in some of the brines in which 8 ounces of sodium hexametaphosphate and 2.62 g. of sodium isoascorbate were added per gallon of solution.

Time and temperature of curing. Artery pumped hams were held in cover pickle for 4, 6, 8 and 10 days at temperatures of 34°, 38°, 42° and 50° F.

Precooking conditions. After hams had been removed from curing, they were soaked in 60° F. tap water for 20 minutes. All hams were heat treated for 18 to 20 hours, until they obtained an internal temperature of 135° F., in a large tunnel dehydrator under constant simulated smoke house conditions; however, the actual smoking was eliminated.

Hams were cut into one-half inch thick slices with bone and fat debris being removed from the surfaces of each slice. Slices were then placed on stainless steel racks ½ inch high in shallow stainless steel pans. Thermocouples, connected to an electronic recording potentiometer, were inserted into the center of the *semimembranosus* muscle of each slice and the pans were tightly covered with heavy duty aluminum foil. Some of these slices were cooked to internal temperatures of 150°, 165° and 180° F. in a 300° F. electric oven while corresponding slices were cooked over a 3-hour period in order that the internal temperature of the meat reached 100°, 125°, and 150° F. at the end of the first, second and third hours, respectively. Oven temperatures during this cooking period were approximately 150°, 170°, and 190° F. for the first, second and third hours.

Preparation of samples for freeze-drying. All bone and visible fat were removed from each slice. The remaining lean meat was cut into pieces approximately 2 in. x 2 in. x ½ in. A composite sample of lean meat was taken from the slices of each ham for moisture determination. The ham pieces were placed in a −18° F. blast freezer for 12 hours before being placed in the freeze-drier.

Freeze-drying. A Stokes vacuum chamber, having 2 hollow shelves (18 inches by 24 inches) fitted for circulating heated water was used for freeze-drying. The chamber was evacuated by 1.5 h.p. Stokes "Microvac" pump equipped with an oil clarifier. Water vapor sublimed from the frozen meat during the drying cycle was condensed in a shell and tube condenser maintained at −20° F. by 1.5 h.p. Freon single stage compressor. Total pressure in the chamber was measured with a Stokes model McLeod Gauge (Flosdorf modification).

Temperature of the shelves was maintained at 120° F. for the first 7 hours and then was gradually reduced to 90° F. for

[a] Technical Paper No. 1224, Oregon Agricultural Experiment Station.

[b] This paper reports research undertaken in cooperation with the Quartermaster Food and Container Institute for the Armed Forces, QM Research and Engineering Command, U. S. Army, and has been assigned number 1011 in the series of papers approved for publication.

[c] Presented at the Nineteenth Annual Meeting of the Institute of Food Technologists, May 20, 1959, Philadelphia, Pennsylvania.

[d] Supplied through the courtesy of Merck and Co., Inc., Rahway, New Jersey.

[e] Supplied through the courtesy of Abbott Laboratories, North Chicago, Illinois.

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Ether Extract	0.049%	Total	3,390. mg. per 100 gm.	Iron	1.90 mg. per 100 gm.
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the remainder of the drying period which was about 9 to 12 additional hours. The chamber pressure during the first 7 hours ranged between 0.6 and 0.7 mm. Hg. and slowly decreased to about 0.25 and 0.3 mm. Hg. toward the end of the drying cycle. Thermocouples were inserted into the samples and connected to a multipoint electronic recording potentiometer.

Samples were freeze-dried until the residual moisture content was approximately 3 to 5% as determined by weight loss.

Storage stability studies. Commercially cured hams were cut into ½ inch thick slices and pre-cooked over a 3-hour period. Final internal temperature of the slices was 150° F. Samples were prepared for freeze-drying according to the procedure mentioned previously. Upon completion of the drying cycle, samples were removed from the drying chamber and approximately 70 g. were placed in No. 307 x 409 C-enameled cans and sealed by one of the 6 following methods:

1. Nitrogen atmosphere + in-package-desiccant (IPD) + activated charcoal
2. Nitrogen atmosphere
3. Carbon dioxide atmosphere + IPD + activated charcoal
4. Carbon dioxide atmosphere
5. Vacuum sealed + IPD + activated charcoal
6. Vacuum sealed

Each IPD included 10 g. of silica gel while 1 g. of activated charcoal was included in another packet.

Cans containing samples that were to be sealed under inert gas were evacuated and flushed twice with the gas and sealed under the third flushing of gas.

Cans of freeze-dried ham were placed in storage at 0°, 70°, and 100° F., although samples canned with IPD and to be stored at 100° F. were first held at 70° F. for 14 days for equilibration of the moisture. For deterioration and organoleptic evaluation, samples stored at 0° F. were analyzed at 6-week intervals while those held at 70° and 100° F. were sampled every 2 weeks over a 12 month period.

As the samples were removed from storage at the designated intervals, the cans were opened and the contents were subjectively examined for odor and color. A 20 g. sample was taken from each can and immediately ground twice in a household food grinder and used for moisture, rancidity and color determinations. Three gram samples were placed in a vacuum oven at 158° F. under a vacuum of 29 inches Hg. for 24 hours and loss in weight was considered as the moisture content. A 2 g. sample was used to determine rancidity by the TBA procedure *(12)*. The remainder of the ground sample was used to measure color by the Hunter Color and Color Difference Meter. The machine was balanced with a standard white plaque having values of Rd 73.3, a − 0.4 and b + 0.5. Since the a/b ratio is directly related to hue, color is reported as a/b ratio.

The remaining intact samples from each can were weighed and then re-canned under 25 inches vacuum. These samples were than vacuum rehydrated by submerging and opening the can under tap water at 120° F. The temperature of the water was maintained at 120° F. during the rehydration period of 5 minutes. Excess water was removed by blotting with paper towels and then the samples were weighed. Rehydration values were calculated as the percentage of the original moisture of the ham.

The rehydrated samples were cooked in steam in a closed vessel until an internal temperature of 180° F. was reached. It was then served to a taste panel consisting of 12 judges, who rated the meat on a hedonic scale for intensity of aroma, color, flavor, juiciness and rancidity. The scale for aroma and flavor was 7, *very pronounced*, to 1, *imperceptible*. Color scale was 7, *dark red*, to 1, *brownish-yellow*. The scale for juiciness was 7, *extremely juicy*, to 1, *extremely dry*, whereas the rancidity scale ranged from 7, *none detectable*, to 1, *very extreme*. Color and flavor were also judged on a desirability basis, with the scale ranging from 9 to 1, with 9 being *very desirable* and 1 being *very undesirable*.

Stabilizers. Slices of commercially cured ham were pre-cooked and prepared for freeze-drying via constant conditions as mentioned previously. Samples were freeze-dried for 18 hours after which they were removed from the drier and instantaneously dipped in one of the following solutions:

1. 0.5% low glucose corn starch solution
2. 1.0% low glucose corn starch solution
3. 1.0% low glucose corn starch solution + 0.01% propyl gallate and 0.5% sodium isoascorbate
4. 0.01% propyl gallate and 0.5% sodium isoascorbate solution
5. 0.015% Santoquin[r] in 95% ethanol solution
6. Control

After dipping, samples were freeze-dried for an additional 3 hours and then canned with CaO as an in-package-desiccant under a vacuum of 25 inches Hg. Samples were held at 70° F. for 14 days for moisture equilibration, after which they were stored at 100° F. for 43 days followed by 20 days storage at 130° F. which approximates 1 year's storage at 100° F. According to the calculations and interpretations of Tappel *et al. (8)* 1 day of storage at 130° F. is about equal to 16 days storage at 100° F. Upon removal from storage samples were analyzed for moisture, rancidity and color by the methods mentioned previously.

RESULTS AND DISCUSSION

Results of many storage stability trials in which freeze-dried ham samples were obtained from hams involved in studies of (a) curing methods, (b) alteration and substitution of curing ingredients and (c) time and temperature of curing, failed to show increased stability beyond that which was obtained with commercially cured hams. Therefore, discussion of these factors will be limited.

Curing methods. Penetration and diffusion of the curing pickle throughout the hams were more uniform and complete, as determined by visual inspection of color development, in the artery pumped hams than in those pumped by the other two methods. Spray pumping was found to be superior to stitch pumping. The main objection to stitch pumping is that the curing solution tends to "localize" where it is injected, thereby resulting in incomplete diffusion of the solution, greater likelihood of spoilage, and uneven saltiness of the cured ham. It was concluded from the studies conducted that artery pumping was the most reliable pumping method as measured in terms of completeness of brine diffusion, and the uniformity in the development of the cured color and flavor.

Alteration and substitution of curing ingredients. In the attempts to produce a ham possessing superior qualities to obtain freeze-dried samples having excellent storage stability properties, the curing ingredients in several experimental brines were varied in concentration or were replaced with other constituents.

Hams cured with pickles having both nitrate and nitrite at levels of 0.195% or more and precooked to an internal temperature of 150° F., showed an excessive amount (over 200 p.p.m.) of residual nitrite, while hams cured in brines having a concentration of both nitrate and nitrite of 0.13% were generally borderline. The developing cured color of hams cured in pickles having low levels of both nitrate and nitrite, 0.065%, was rather incomplete and irregular. In most cases, the color that did develop was somewhat unstable. Consistently good results were obtained with

[r] Supplied through the courtesy of Monsanto Chemical Co., St. Louis, Mo.

a pickle containing 0.15% nitrate and 0.09% nitrite which was used as the control pickle.

Taste panel results indicated that hams pumped with brines having low salt levels, 20° and 40° salometer, and Sucaryl in place of sugar, were about equal in flavor and color as the hams cured in the control brine; however, freeze-dried samples from hams cured in these experimental brines showed very poor stability after 4 to 6 weeks storage at 100° F. Rehydrated freeze-dried samples from hams cured with brines having low salt levels were found to be devoid of cured flavor or spoiled. Apparently, salt levels of the 20° and 40° salometer pickles were not high enough to preserve the ham. Reconstituted freeze-dried samples from hams cured in brines containing Sucaryl were considered by the taste panel to have a flavor somewhat foreign to that which is characteristic of normal cured ham.

Additions of 2.62 g. of sodium isoascorbate and 8 ounces sodium hexametaphosphate per gallon of pickle appeared to exert a beneficial effect upon cured color retention of the stored freeze-dried samples.

Time and temperature of curing. A curing time of 6 days was found to be the optimum length of curing at a temperature of 38° F. Curing at temperatures of 42° and 50° F. for 4 days produced hams having considerable variation in flavor. An off-flavor was evident in some of these hams and it became more undesirable as the length of curing time increased. The development of the off-flavor can probably be attributed to the growth of undesirable microflora at temperatures of 42° and 50° F. Hams cured at a temperature of 34° F. for 6 days were generally lacking in flavor and the developing cured color was quite irregular, although improvements were noted as length of curing time increased.

Precooking. Ham slices cooked over a 3-hour period in which the internal temperature of the meat reached 100° F., 125° F. and 150° F. at the end of the first, second and third hours, respectively, were judged by the taste panel to be superior in color retention and more flavorful than the slices cooked to internal temperatures of 150°, 165° and 180° F. in the much shorter time of 20 to 30 minutes. Rehydrated freeze-dried samples from these treatments were also rated in this manner. Therefore, the 3-hour cooking procedure, as mentioned above, was the method of precooking all of the samples for storage stability tests of freeze-dried ham.

Storage stability. Upon the initial opening of the cans of freeze-dried ham as they were removed from storage, a pungent and burnt odor, which sometimes was accompanied by a stale and rancid odor was found to be characteristic of the samples stored without activated charcoal. Samples sealed under nitrogen or CO_2 seemed to have more disagreeable odors than those that were vacuum packed. These off-odors were practically non-detectable in the samples stored with charcoal, regardless of the method of pack.

After 6 weeks of storage at 70° and 100° F., the color of the dried samples began to change from reddish-pink to pinkish-tan; the change was most evident in samples stored at 100° F. At the end of 12 weeks of storage, a number of dried samples stored at 70° F. were observed to be tan or brownish-yellow while those stored at 100° F. showed a variety of discolorations, such as cream or beige with orange and yellow tinge; however, the intensity of off-odor and discolorations diminished considerably after rehydration.

In comparing the results of the taste panel evaluation and the objective determinations of samples packed under nitrogen or CO_2 to those canned under vacuum, it appears that vacuum packed samples were slightly superior to those packed under an inert atmosphere. The most noticeable differences are shown by the values for both color and flavor desirability and intensity of rancidity which are listed in Table 1.

TABLE 1

Results of taste panel and objective measurements of rehydrated freeze-dried ham stored under inert gas or vacuum for varying periods of time

Method of pack	Length of storage (weeks)						
	0	6	12	18	20	22	24
Color desirability							
Nitrogen	7.0	6.4	5.1	5.3	5.0	4.4	....
CO_2	6.9	5.6	5.6	5.2	5.1	4.6	....
Vacuum	7.3	7.1	6.5	5.6	4.5	4.8	5.4
a/b color ratio							
Nitrogen	1.65	.96	.76	.84	.89	.77	....
CO_2	1.47	1.06	.84	.78	.83	.84	....
Vacuum	1.71	1.11	1.00	1.03	1.08	1.17	1.10
Flavor desirability							
Nitrogen	7.0	5.5	5.4	5.0	4.9	4.8	....
CO_2	6.8	5.3	5.1	5.4	5.1	4.7	....
Vacuum	7.2	6.9	6.0	5.8	5.9	5.4	4.6
Rancidity							
Nitrogen	6.7	5.0	5.3	5.2	5.2	4.9	....
CO_2	6.7	5.2	5.2	5.1	5.1	5.0	....
Vacuum	6.9	6.2	5.5	5.6	5.9	5.7	5.7
TBA values (535 mμ)							
Nitrogen	.27	.34	.29	.33	.32	.39	....
CO_2	.22	.32	.26	.38	.28	.42	....
Vacuum	.20	.28	.26	.32	.21	.38	.28
Juiciness							
Nitrogen	5.3	4.6	4.5	4.7	4.6	4.2	....
CO_2	5.4	4.5	4.5	4.8	4.2	4.3	....
Vacuum	5.4	5.0	4.7	4.6	3.9	4.2	3.0
% rehydration							
Nitrogen	89.4	86.7	83.5	85.1	86.2	75.1	....
CO_2	88.9	85.0	85.4	82.7	86.4	78.6	....
Vacuum	88.4	86.1	88.2	85.1	85.9	78.1	65.3

The taste panel found that the rehydrated vacuum packed samples retained more desirable color and flavor, and were scored slightly less rancid than those packed under nitrogen or CO_2. After 20 weeks of storage at both 70° and 100° F., nitrogen and CO_2 packed samples were considered to be beyond the normal range of acceptability. At this time, panel members commented that the aroma and flavor of the rehydrated samples which were packed under inert gas were quite foreign to that of cured ham. The flavor was difficult to describe, although it was considered not to be very rancid. Sharp *(6)* has found that freeze-dried pork will deteriorate during storage even in the absence of oxygen and that the bitter, burnt flavors are produced by the reaction of the sugar fraction in meat with the non-protein fraction.

Since the taste panel data and the TBA values indicate that the vacuum packed samples were less rancid than the inert gas packed samples, the method of gas sealing employed in this study may not have removed

as much of the atmospheric oxygen as was removed by sealing under vacuum. Therefore, the amount of residual oxygen remaining in the cans under inert gas may have been appreciably higher than that in the vacuumized cans, thereby causing a slightly increased rate of oxidative rancidity.

Only slight differences in juiciness and level of rehydration were shown between samples of the different packs stored at 0°, 70° and 100° F. Most of these differences can probably be attributed to the difficulty in maintaining heterogeneity among the samples, as will be discussed later in the paper.

Although the taste panel found the vacuum packed samples stored at either 70° or 100° F. to be fairly acceptable after 22 weeks of storage, similar samples stored for 24 weeks were judged as unacceptable. Taste testing of the samples stored for this study was discontinued after 6 months of storage, although the remaining samples were subjectively examined periodically. One of the vacuum packed samples stored for 8 months at 100° F. exhibited excellent stability. It had retained a desirable reddish-pink color with almost no visible browning and off-odor was practically non-existent. After rehydration, the meat was rated by the taste panel who stated that the flavor, color, juiciness and texture were very desirable and only a slight degree of rancidity could be detected.

Generally, samples stored at 70° F. were rated slightly higher than corresponding samples held at 100° F. These data are presented in Table 2.

Color and flavor desirability of freeze-dried ham are the factors apparently affected the most by an increase in moisture content and also by an increase in storage temperature as shown in Table 3. Samples stored with the higher amounts of moisture (in excess of 7.5%) and held at 100° F. showed a greater degree of discoloration than similar samples stored at 70° F.

Within each moisture group, samples that were stored at 70° F. and rehydrated were scored by the taste panel at least one-half unit higher, on a 9 point scale, in color desirability than the samples held at 100° F. Rehydrated meat from samples having a residual moisture content above 7.5% during storage were rated by the taste panel from one-half unit to one and one-half units lower than the samples stored with moisture contents below 7.5%. This same trend was also noted with flavor desirability, although the differences were not as great.

TABLE 2

Results of taste panel and objective measurements of rehydrated freeze-dried ham stored at different temperatures for varying periods of time

Storage temperature	Length of storage (weeks)						
	0	6	12	18	20	22	24
Color desirability							
0° F.	7.3	5.9	6.0	5.3	....	....	7.0
70° F.	8.0	6.7	6.2	6.1	5.8	5.0	4.2
100° F.	7.7	6.2	5.1	4.7	3.9	4.2	3.9
a/b color ratio							
0° F.	1.51	.98	1.14	1.00	....	....	1.05
70° F.	1.64	.99	.92	.81	1.07	.99	1.10
100° F.	1.66	1.00	.81	.97	.79	.86	1.39
Flavor desirability							
0° F.	7.0	5.8	4.4	5.1	....	....	5.4
70° F.	7.1	6.1	5.4	5.8	5.6	5.1	4.5
100° F.	7.1	5.6	5.6	5.0	5.0	4.8	4.6
Rancidity							
0° F.	6.9	5.3	4.3	5.0	....	....	5.0
70° F.	6.6	5.8	5.5	5.4	5.4	4.9	5.7
100° F.	6.7	5.5	5.3	5.3	5.3	5.5	5.8
TBA values (535 mμ)							
0° F.	.25	.55	.35	.46	....	....	.3_
70° F.	.19	.29	.26	.37	.28	.35	.32
100° F.	.24	.28	.26	.31	.26	.44	.23
Juiciness							
0° F.	5.2	5.2	5.1	4.8	....	....	3.4
70° F.	5.2	4.6	4.6	4.6	4.5	4.0	2.7
100° F.	5.0	4.7	4.4	4.7	4.0	4.3	3.3
% rehydration							
0° F.	90.1	89.7	86.4	92.7	....	....	69.3
70° F.	88.3	86.2	85.8	81.1	85.6	75.1	55.6
100° F.	89.7	85.0	85.2	83.4	86.7	79.4	75.0

Cured ham that was vacuum packed and held at 0° F. for 20 weeks and rehydrated freeze-dried ham from vacuum packed samples stored for the above length of time at both 70° and 100° F. were compared by the taste panel against samples of recently cured ham. It is interesting to note, in Table 4, that the rehydrated freeze-dried samples stored at 70° F. were about as acceptable, flavorwise, as were the non-dehydrated ham samples held at 0° F.; however, neither of these samples was rated as high in flavor desirability as the recently cured ham. From the standpoint of color, the freeze-dried samples stored at both 70° and 100° F. were decidedly inferior to those of frozen and recently cured ham.

Stabilizers. It was believed that by dipping partially dried samples in solutions containing various stabilizers that some of the solution would penetrate into the porous structure and upon further drying would leave a protective coating on the dried exposed surfaces which would aid in retarding the developing rancidity and, perhaps, browning.

Results of TBA determinations and the a/b ratios,

TABLE 3

The effect of moisture on the characteristics of freeze-dried ham stored for 22 weeks

Storage temperature	No. of samples	% residual moisture	Intensity		Desirability		TBA 535 mμ	a/b color ratio	% rehydration
			Juiciness	Rancidity	Flavor	Color			
70° F.	14	4.4	4.7	5.4	5.8	6.4	.33	.99	85.5
100° F.	16	4.2	4.6	5.2	5.5	5.9	.30	.96	83.6
0° F.	9	6.4	5.2	5.2	5.6	5.7	.50	1.06	90.3
70° F.	30	6.3	4.7	5.6	6.0	6.5	.29	.93	85.2
100° F.	21	6.2	4.6	5.6	5.2	5.4	.28	.95	85.7
0° F.	8	8.1	4.9	4.3	4.3	5.5	.42	1.03	89.0
70° F.	10	8.7	4.5	5.6	5.7	5.9	.27	.89	84.9
100° F.	11	8.6	4.4	5.2	5.0	4.4	.28	.71	84.2
70° F.	6	11.4	4.5	5.4	5.4	4.9	.31	.70	81.9
100° F.	10	11.1	4.5	5.5	5.3	4.5	.24	.94	85.4

TABLE 4

Comparison of flavor panel scores of rehydrated freeze-dried ham with non-dehydrated frozen ham and recently cured ham

Description of samples [1]	Intensity				Desirability	
	Flavor	Juiciness	Color	Rancidity	Color	Flavor
Freeze-dried						
Vac Pak, 20 wks. storage at 70° F.	4.5	4.3	4.9	6.2	5.6	6.7
Vac Pak, 20 wks. storage at 100° F.	4.4	3.5	3.2	5.7	3.4	5.2
Frozen non-dehydrated						
Vac Pak, 20 wks. storage at 0° F.	4.7	5.6	5.0	6.4	8.2	6.8
Recently cured ham (No storage)	5.6	5.6	5.4	6.6	8.1	8.0

[1] Two samples per treatment.

which are shown in Table 5, show that little effect was derived from the stabilizers used.

In other attempts to prolong the storage stability of freeze-dried ham, experiments were devised to determine whether filling the drying chamber at the end of the drying period with inert gases, rather than with air, would have any beneficial effect upon the stability of the stored product. It was hypothesized that by infusing inert gas into the chamber while simultaneously releasing the vacuum at the end of the drying cycle, some of the gas would enter into the pores of the meat and more or less be trapped and retained in place of air. If such were the case, then this scheme, plus packing under inert gas or vacuum, should help retard the developing rancidity by decreasing the amount of atmospheric oxygen coming into contact with the meat. Preliminary results show that lower TBA values were recorded for stored samples taken from loads that were removed from the drying chamber in the above manner than for the stored samples from loads in which air was inserted at the time of vacuum release. Although these differences were not statistically significant, the pattern of the values indicate that the infusion of an inert gas with simultaneous releasing of the chamber vacuum had the tendency to exhibit some protective action; however, further work is needed in this area to determine the value of this procedure in long term storage.

Rehydratability. During the long term storage study, considerable differences were noted between freeze-dried samples subjected to similar, if not constant, treatments and storage periods. Although attempts were made to maintain a degree of homogeneity among the samples, the inherent differences between certain muscles of a ham make it difficult to obtain a number of ideal homogeneous samples. Therefore, cured hams were boned and the muscles were segregated into the following four general groups for convenience: (1) *semimembranosus;* (2) *biceps femoris;* (3) *semitendinosus;* and (4) knuckle or tip muscles. All samples were precooked and freeze-dried via a constant and standard procedure. Samples were rehydrated by placing them in boiling water for 20 minutes, after which they were evaluated by the trained taste panel. The results of this evaluation are listed in Table 6.

The knuckle muscles absorbed 14 to 18% more water than did the other muscles; however, this magnitude of difference in rehydration did not seem to be detected to any great extent by the taste panel. Samples of rehydrated knuckle muscles were rated 0.8 to 1 unit higher for juiciness than were the *semimembranosus* and *biceps femoris* muscles, respectively. Difference in the juiciness score between the knuckle muscle and the *semitendinosus* were nil.

It was observed on a number of occasions that the rehydrated samples in which the muscle fibers lay parallel with the largest surface area were considerably drier and tougher than the samples having the fibers in a perpendicular position. Auerbach *et al. (1)* reported that perpendicular fibered freeze-dried beef samples had a significantly higher level of rehydration than the samples having the muscle fibers parallel to the surface. Therefore, an experiment was carried out to determine the effect of the muscle fiber orientation, per muscle group, upon the rehydratability of freeze-dried ham. The results are shown in Table 7.

In comparing the panel scores, it is interesting that there was little apparent difference between the perpendicular and parallel fibered samples of the knuckle muscle. Although the perpendicular fibered samples of this muscle absorbed about 6% more water than

TABLE 5

Effect of stabilizers on the stability of freeze-dried ham stored under accelerated conditions to equal one year's storage at 100° F.

Treatment [1]	% Residual moisture	a/b color ratio	TBA 535 mμ
1. 0.5% low glucose corn starch solution	3.28	1.13	.339
2. 1.0% low glucose corn starch solution	2.00	1.06	.335
3. 1.0% low glucose corn starch + 0.01% propyl gallate + 0.5% sodium isoascorbate solution	2.24	1.11	.326
4. 0.01% propyl gallate + 0.5% sodium isoascorbate solution	2.40	1.15	.331
5. 0.015% Santoquin in 95% ethanol solution	2.17	1.02	.347
6. Control	1.74	1.11	.333

[1] Eleven samples per treatment.

TABLE 6

Rehydratability of freeze-dried ham samples from different muscles

Muscle group [1]	Intensity	Desirability		% Rehydration
	Juiciness	Color	Flavor	
Semimembranosus	3.7	7.4	6.6	52.3
Semitendinosus	4.4	6.9	6.6	54.7
Biceps femoris	3.5	6.6	6.3	50.8
Knuckle or tip	4.5	6.9	6.8	69.1

[1] Six samples per group.

TABLE 7

Effect of muscle fiber orientation on the rehydratability of freeze-dried ham samples from different muscles

Muscle group	Orientation[1] of muscle fibers	Intensity	Desirability		% Rehydration
		Juiciness	Color	Flavor	
Semimembranosus	Parallel	3.6	6.9	7.0	64.7
	Perpendicular	4.5	7.8	7.5	71.4
Semitendinosus	Parallel	3.2	6.6	5.5	62.3
	Perpendicular	4.1	6.8	6.6	60.7
Biceps femoris	Parallel	3.9	6.3	5.8	56.4
	Perpendicular	4.6	6.7	6.7	66.2
Knuckle or tip	Parallel	5.7	6.6	7.5	73.3
	Perpendicular	5.3	6.7	7.4	79.3

[1] Two samples per fiber group.

the samples having parallel fibers, the panel rated the latter as being juicier. The parallel fibered samples of the *semitendinosus* absorbed slightly more water than the perpendicular fibered samples; however, in this instance, the panel score for the parallel fibered samples was 0.9 of a unit lower than that for the perpendicular fibered samples. With the other two muscles, the perpendicular fibered samples absorbed more water and were rated juicier than those having the parallel fibers. Flavor desirability appears to be affected by the level of rehydration. Samples scored by the panel as being juicier (generally, the perpendicular fibered samples), were also scored higher in flavor desirability. Rehydratability is largely affected by structural interference, size of interfibral space *(10)*, and also by the rate of swelling of the outer layers of the meat *(4)*.

Another point of interest is that freeze-dried samples vacuum rehydrated for 5 minutes in 120° F. water had an average rehydration level of 85.6% (135 samples) as compared to an average of 66.5% (85 samples) for those reconstituted without vacuum.

SUMMARY

Experiments were conducted in which (a) curing methods, (b) alteration and subsitution of curing ingredients, (c) time and temperature of curing and (d) precooking conditions were modified in an attempt to produce a ham possessing superior qualities to obtain freeze-dried samples having excellent storage stability properties. Results of these investigations failed to show increased stability beyond that which may be obtained with commercially cured hams used in these studies.

Deterioration of freeze-dried ham during storage reflects directly upon the acceptability of the product. Color and flavor are the quality factors most adversely affected by storage at elevated temperatures. Stability of the stored samples is also affected by the moisture level. A combination of high moisture content and high storage temperature produced the most detrimental changes.

Results of studies reported here show that packaging the freeze-dried product in vacuumized cans has been superior to packaging in cans filled with nitrogen or carbon dioxide. Flavor panel results indicate that vacuum packed samples retained their acceptability for 5½ months when stored at 70° or 100° F.

Use of those stabilizers which have been tested appears to have little effect on prolonging the storage stability of freeze-dried ham.

Rehydration results of different freeze-dried ham muscles indicate that the muscles do not possess an equal water absorption capacity. The knuckle or tip muscles show the highest level of rehydration.

Rehydratability is also affected by the muscle fiber orientation. Freeze-dried samples having the muscle fibers in a perpendicular position to the largest surface area absorbed more water and were rated juicier than the samples having the parallel fibers.

Acknowledgments

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A Gas Chromatographic Method for Determining Gases in the Headspace of Cans and Flexible Packages

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(Manuscript received June 17, 1959)

THE PACKAGING OF FOOD MATERIAL, utilizing inert gases for the prevention of quality deterioration, has been practiced successfully for many years. Although it is generally agreed that the determination of the concentration of these gases is of extreme importance *(2, 4)*, no practical methods are available which encompass the wide range of packages one encounters.

As is commonly known, the orsat method, generally used throughout the food industry, requires a large volume of sample, is time consuming, and, when reduced to a micro scale, becomes extremely complicated. Commercial oxygen analyzers require smaller sample volumes, but are limited to the analysis of oxygen. Gas chromatographic methods, however, require less than 1 ml. of gas for satisfactory analysis, are extremely rapid, and quite versatile *(1, 3, 5, 7)*.

The procedure used successfully for several months in our laboratory employs a simple sampling method which can be adapted to any container, followed by gas chromatographic analysis.

APPARATUS

Chromatographic equipment. Any conventional gas chromatography apparatus may be used for this procedure. In our case, a 10-foot, ¼-inch O.D. stainless steel column is coiled helically to fit a dewar flask (diam. 16¼ cm.) which acts as an air bath stabilizing the column temperature. The column is attached to a Gow Mac Instrument Company thermal conductivity unit. The bridge output signal from the detector is applied to an 0–10 mv strip chart recording potentiometer. The sample inlet is a rubber seal, which allows the use of a hypodermic syringe. Helium is used as a carrier gas at a flow rate of 50 ml./min.

For determining oxygen and nitrogen, the column is filled with Linde Molecular Sieves, Type 13X. Air and carbon dioxide may be determined by using a column packed with activated silica gel. Some workers arrange these columns in series with a suitable arrangement of valves and are able to analyze not only O_2, N_2, and CO_2 but several other gases in a single determination *(3, 5, 7)*.

Can-piercing device. A Zahm Air Tester [a] was modified as follows: The pressure gauge was replaced by a metal socket [b] (8 mm. long and 6 mm. diameter) into which a rubber seal [b] was inserted. Figure 1 illustrates this modified piercing device.

Gas transferring syringe. A standard 1 ml. syringe fitted with a small metal stopcock [c] and a No. 22⅝" hypodermic needle is adequate. Specifically, we have obtained best results with a Vim No. 200 [d] 1-ml. syringe which has a stainless steel plunger. The joints connecting the syringe, stopcock and needle are coated with a resin or heavy grease to avoid any possible gas leakage. The metal stopcock is only necessary for sampling vacuum packed containers.

[a] Zahm and Nagel Company, Inc., Buffalo, N. Y.

[b] Burrell Corporation, Pittsburgh, Pa.—Cat. No. 274-6.

[c] Becton Dickinson & Company, Rutherford, N. J.—Cat. No. M501.

[d] MacGregor Inst. Co.

SAMPLING

Flexible packages. A one-inch square of inner-tube patch material is glued to the package with rubber cement. When the cement has dried, a syringe is inserted through the patch without causing the package to tear or leak. The syringe, after being filled to the desired volume, is removed; the rubber patch reseals the hole and the package can be used for resampling, if desired. The contents of the syringe are injected into the gas chromatography apparatus.

Cans. The can-piercing device (Figure 1) is centered over the can and a thin layer of grease is smeared on the can at the spot where the rubber seal will make contact. The device is lowered until a good seal is made between the rubber and the can (A) but the can is not pierced. The needle valve (B) is connected to a water aspirator, the chamber evacuated to

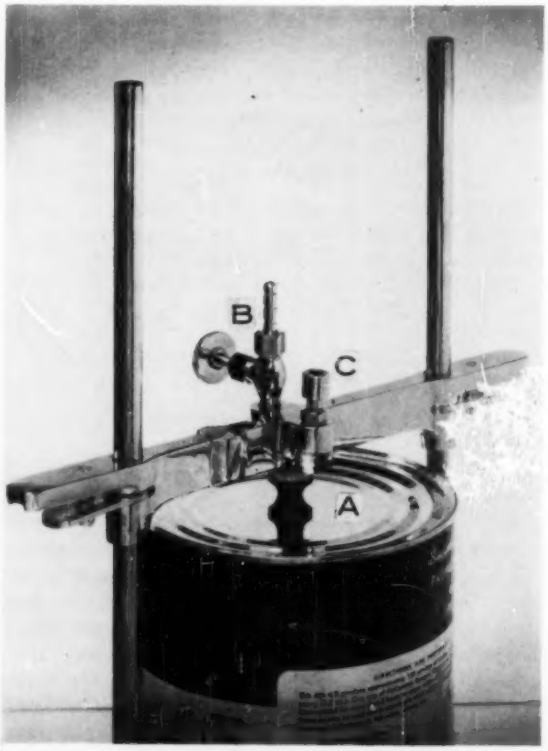

Figure 1. Modified can piercing device.

20 mm. Hg and the needle valve closed. The can is then pierced, a sample is removed with a syringe through the rubber seal (C) and injected into the gas chromatography apparatus.

Vacuum packed containers. Any container which is under a vacuum may be sampled in a manner somewhat similar to that described. It is necessary that the stopcock be attached to the end of the syringe. After the syringe has been filled, and before it is removed from the container, the stopcock is closed and the plunger allowed to slide down the syringe until the pressure is equalized. The syringe is removed from the container and the plunger pushed down until a slight positive pressure is attained inside the syringe. When the stopcock is opened, a small amount of sample is ejected from the syringe, displacing residual air which has collected in the needle, and the remaining sample is injected into the gas chromatography apparatus.

Calculations. The quantitative interpretation of the chromatogram is based on the peak area, which can be measured in several ways *(6)*. We prefer to multiply the peak height by the width at half height. Then:

$$\frac{\text{Area A}}{\text{Area A} + \text{Area B}} \times 100 = \% \text{ A}$$

A typical chromatogram is shown in Figure 2. The oxygen analysis as obtained by this technique is always high by approximately 4% since argon is not separable from oxygen under these conditions. For example, a value of 4% oxygen as calculated from a chromatogram is actually 3.84%. These

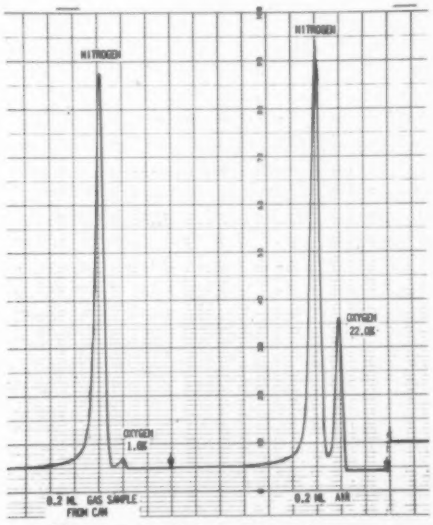

Figure 2. Typical gas chromatograms.

calculations assume that the differences in the thermal conductivities of the gases being analyzed are negligible as compared with that of the carrier gas. This assumption introduces a slight error which can be corrected by calibrating the thermal conductivity cell *(8, 9)*. The experimenter can make these corrections, but it is our opinion that this type of accuracy is not justified, since the measurement of flavor is determined by subjective means: the taste panel.

RESULTS AND DISCUSSION

Analyses of standard oxygen-nitrogen mixtures obtained by both gas chromatographic and orsat methods are presented in Table 1. Although the precision of the two methods is about equal, the gas chromatographic method has greater accuracy. Moreover, the

TABLE 1

Comparative analysis

% Oxygen		
Mass spectrometry[1]	GC analysis[2]	Orsat analysis[2]
8.98	8.91 ± 0.10	10.50 ± 1.20
3.99	4.05 ± 0.10	4.17 ± 0.07
0.97	1.05 ± 0.04	1.07 ± 0.11

[1] The analytical standard.
[2] Average of 4 determinations.

gas chromatographic analysis is completed in 7 minutes with less than 0.5 ml. of sample, whereas the orsat method usually requires a minimum of 25 ml. of sample and takes longer than an hour for complete analysis.

The results of experiments conducted to investigate the reproducibility of analysis upon repetitive resampling are shown in Table 2. The cans were placed on the piercing device, sampled and allowed to remain intact for 18 hours after which they were resampled. Flexible packages were sampled and resampled over the same period of time and in no case was any significant difference observed. Results in Table 2 are typical of many which have been obtained from all sorts of containers, including vacuum packed cans and packages.

TABLE 2

Per cent oxygen in dry powdered food products

Container	Time of sampling and resampling, hours	% O_2
Can, 608 x 906	0	2.2
	18	2.0
Can, 603 x 700	0	1.9
	18	2.2
Flexible package, 4¾″ x 6¼″	0	7.6
	18	7.4

SUMMARY

A method for determining gases in the headspace of cans and flexible packages is given which allows analysis on not more than 0.5 ml. of gas, requires 7 minutes per determination, can be run by a technician, and is sufficiently accurate for the purpose intended.

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Derivation of a New Formula for Computing Raw Tomato Juice Color from Objective Color Measurement[a]

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(Manuscript received May 21, 1959)

Color is probably the most useful single criterion for evaluating the quality of tomato fruit for processing. Thus, an accurate determination of the color of the fruit or a puree made therefrom is of prime benefit in assigning a quality grade.

Numerous workers *(1, 2, 3, 4, 5, 8, 12, 13)* have proposed various color indices to define or characterize the color of raw or processed tomato juice and other commodities.

Pomerantz, Goldblith and Proctor *(12)* and Robinson *et al. (13)* specified color indices based on abridged spectrophotometry as well as tristimulus evaluation which they found best expressed the color of processed tomato juice.

Gould *(4)* suggested that a single-wavelength instrument differentiated samples of tomato juice as to color.

Younkin *(18)* pointed out the limitation of one-dimensional measurement and the validity of consideration of all 3 attributes of color specifications, hue, lightness and saturation.[b] He also pointed out that a color index that will separate one group of samples may be inadequate for another group of samples if the index is limited to incomplete color characterization.

MacGillivray *(10)* was one of the first to describe a color index based on the Munsell color system.

Nickerson *(11)* later implemented the technique of disk colorimetry to a point where, in the case of tomato product color evaluation, a series of Munsell disks was developed and specified for the various tomato products. Disk colorimetry is still widely used by the U. S. Department of Agriculture in the evaluation of the color of processed tomato products.

In 1948, Hunter *(6)* reported a photoelectric color-difference meter that measured color by the use of 3 filters approximating the X, Y, and Z functions of the C.I.E. system. His Color and Color-Difference Meter represented a departure from usual colorimeters as it afforded data in a form closely related to the spacing of the Munsell system.

Yeatman and Sidwell *(17)* reported developmental research by the U. S. Department of Agriculture in connection with the use of the Munsell disks for raw tomato juice visual scoring and the relationship of various objective color measurements with these visual scores. In studies conducted in 1956 *(17)*, it was reported that observers may differ materially in their judgment of samples of raw tomato juice. To some observers, lightness might be the primary aspect of color to be judged. On the other hand, hue and saturation may be considered to be most indicative of differences between samples to certain other observers. However, the normal observer sees color in its 3-

[a] Presented at the Nineteenth Annual Meeting of the Institute of Food Technologists, May 20, 1959, Philadelphia, Pennsylvania.

[b] *Hue* is that attribute of color associated with the sensation of redness, yellowness, blueness, etc. *Lightness* (or value) is associated with the brightness aspect of color and usually depends on the relative luminous flux transmitted or reflected by the colorant. *Saturation* (or chroma) is the attribute associated with the strength of hue or freedom from admixture with white, grey, or black.

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dimensional aspects of hue, lightness, and saturation.

The close relationship of the Munsell color space and the Hunter-chromaticity diagram made these two systems especially applicable for use in the region and specification of raw tomato juice color in the present work.

Any tomato-color index that may be adopted for general use should be sufficiently versatile to indicate differences between samples of purees derived from fruits ripened under a wide variety of conditions which cause substantial differences in color specification.

The derivation of a new formula for computing raw tomato juice color, its development and substantiating theory, is the subject of this paper.

EXPERIMENTAL

Experienced personnel trained in raw tomato inspection or tomato-juice grading evaluated raw tomato juice samples using standardized Macbeth-Munsell Disk Colorimeters.[c] (Figure 1). All of the observers visually scored the individual samples under standardized conditions of daylight illumination provided by the disk colorimeter and at 45° angle of viewing with incident light perpendicular to the viewing surface. Each of the observers had passed the Inter-Society Color Council Color-Aptitude Test, the Glenn Color Rule Test, and the Ishihara Color Blindness Test showing them to be acceptable subjects for this work.

All visual color scorings were made with the guidance of a series of carefully prepared Munsell disks having regularly spaced color attributes of hue, lightness, and saturation in the region of raw tomato juice color. Munsell renotations for the disks are shown in Table 1. Hunter L, a_L and b_L values for respective disks are included.

These disks were prepared similarly to those described by Wilson and Dever *(15)*, but corrected for regularity of the 3 color attributes. Arbitrary values from 10 to 30 in increments of 5 units were assigned the disks. The respective color specifications of the 10 and 20 disks have close relationship to minimum U. S. No. 2 color tomatoes and minimum U. S. No. 1 color tomatoes as specified in the U. S. Standards for the Manufacture of Strained Tomato Products *(14)*.

A series of 5 disks was used in experiments conducted during the first year of the work (1958), and direct-comparison match, interpolation or extrapolation could be made between disks and samples in assigning visual scores. A series of 7 disks was used during the second year of work (1959). The additional 2 disks were assigned values of 5 and 35 score value, respectively, to extend the range in color space afforded by these disks, thus avoiding extrapolation.

The raw tomato juice samples were prepared from frozen whole tomatoes of 3 varieties—Roma, Rutgers, and Garden State. Tomatoes of each variety were selected at harvest for freedom from defects, segregated according to low, medium and high color, then frozen immediately at −10° F. Fruit prepared in such a manner have been held at −10° F. for as long as 1½ years with good color retention. Tomato juice processed from frozen whole tomatoes has been found to be highly acceptable by taste panel evaluation *(16)*.

The samples were prepared by first thawing the frozen fruit then extracting them with a laboratory-type Enterprise Meat and Food Chopper with a juice attachment having a .034-inch mesh screen. Blends of the extracted samples were made to achieve a wide gamut in color space, but not beyond the range of tomato juice colors commonly encountered. All samples were kept in cups in an ice bath or in viewing cups in a refrigerator at approximately 40° F. throughout each test.

Objective color measurements were made on all juice samples with the Gardner Automatic Color and Color-Difference Meter in terms of C.I.E. trichromatic coefficients of *X*, *Y*, and *Z* and Hunter L, a_L and b_L. Tomato-red ceramic tiles used to standardize the Color and Color-Difference Meter in 1958 and 1959 had assigned C.I.E. values of X = 10.9, Y = 7.0, and Z = 2.5; and X = 9.3, Y = 6.1, and Z = 2.3, respectively. Hunter values were L = 26.5, a_L = 26.9 and b_L = 12.9; and L = 24.7, a_L = 24.2 and b_L = 11.7, respectively, for the 2 tiles. Assigned coefficents were based on values derived from complete spectrophotometric reflectance curves made on G. E. Recording Spectrophotometers.

An abridged spectrophotometer, the IDL-Color Eye, was also used to characterize all samples in terms of spectral-reflectance curves relative to a white vitrolite standard calibrated in terms of MgO.

In a typical experiment the juice samples were prepared and their color measured objectively with the various instruments and the results recorded. The individual observers then scored each juice sample in the manner prescribed. At no time did the observers have knowledge of the results of objective color measurements. Visual scores were then compared to and correlated with the objective color readings. From 3 to 6 observers participated in each of the experiments.

Statistical methods were those of Li *(9)*. All correlations are significant at the 0.01 level unless otherwise indicated.

RESULTS AND DISCUSSION

It does not seem practicable to relate the detailed results of all the experiments. Therefore, we select one of the experiments of the 1958 studies as representative. This is Experiment 4 in these tests.

When the color readings of the samples in this experiment were plotted in Hunter-Munsell color space, a rough triangle was created. Figure 2 is a graphic representation of the array of the samples in Experi-

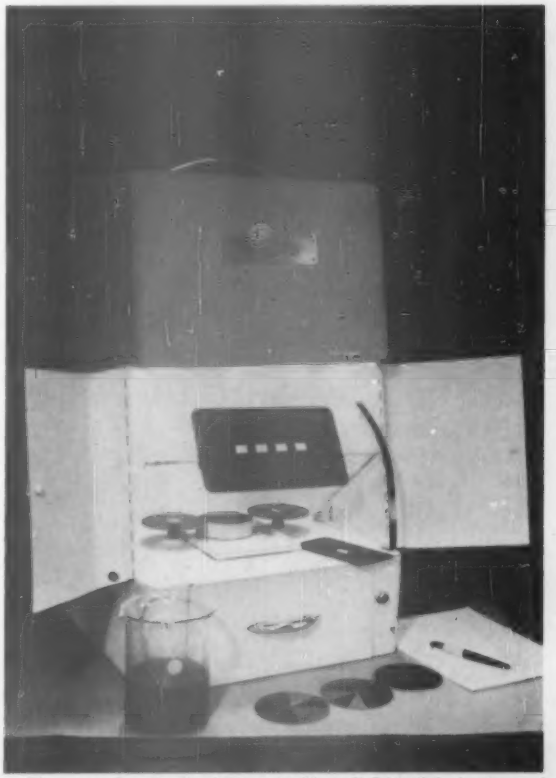

Figure 1. Standardized Macbeth-Munsell Disk Colorimeter and Munsell disks used in visual scoring of raw tomato juice color.

[c] Mention of this or other commercially manufactured instruments does not constitute endorsement or recommendation by the U. S. Department of Agriculture.

TABLE 1

Specifications of Munsell disks for raw tomato juice, 1958–59

Score	Munsell components in percent [1]						Munsell renotation for mixture		Hunter		
	R1	R2	R3	YR	N1	N4			L	a_L	b_L
35[2]	25.0	30.0	45.0	.....	.....	.....	6.84R	2.76/9.75	23.56	35.20	10.99
30	.....	.....	100.0	.....	.....	.....	7.40R	2.92/9.50	24.89	33.96	11.95
25	.....	.....	93.2	3.7	3.1	.....	7.75R	3.00/9.31	25.63	32.71	12.59
20	.....	.....	89.0	7.1	2.6	1.3	8.29R	3.14/9.10	26.79	31.81	13.14
15	.....	.....	71.5	14.0	9.6	4.9	9.18R	3.31/8.38	28.34	28.22	13.56
10	.....	.....	51.7	21.0	14.0	13.3	9.83R	3.56/7.39	30.54	23.89	13.43
5[2]	.....	.....	43.0	32.0	12.5	12.5	0.89YR	3.85/7.64	33.24	24.05	15.75

[1] Munsell renotations for components: R1 = 7.2R 2.06/7.7; R2 = 7.8R 2.08/12.0; R3 = 7.4R 2.92/9.5; YR = 3.0YR 5.14/11.2; N1 = N 0.50/PB0.4; N4 = N 4.05/BG0.05. The C.I.E. specifications for the components are: (R1): X = .0580, Y = .0329, Z = .0185; (R2): X = .1260, Y = .0645, Z = .0130; (R3): X = .1081, Y = .0620, Z = .0230; (YR): X = .2842, Y = .2101, Z = .0402; (N1): X = .0057, Y = .0058, Z = .0086; (N4): X = .1206, Y = .1235, Z = .1467, respectively.

[2] Disks added in 1959 to extend scale in color space thus avoiding extrapolation.

ment 4. This triangle ACB must be visualized in 3-dimensional aspect as it is plotted at Munsell-value 3 level. Samples as high as value 3.3 and as low as 2.5 actually occurred.

The relative positions of the regular Munsell disks used to guide the observers' decisions in scoring are also shown in Figure 2. Here again, the positions of the disks are plotted at value 3 level, but they should be visualized in 3-dimensional space.

The triangle loci represent Hunter L values from 21.9, 28.3, and 27.0; and a_L/b_L ratios of 2.39, 1.38, and 1.97, respectively. Along the side CB of the triangle, essentially only hue and saturation changes occur with only slight lightness change. Along the side BA, lightness and saturation changes predominate. Along the side AC, there are changes in hue and lightness, with only slight saturation change. The respective L, a_L/b_L ratios and average visual scores for the samples studied in Experiment 4 are shown in Table 2.

Although a number of color samples in this array and in other experiments had nearly identical Hunter L values and others had nearly identical a_L/b_L ratios, the observers did not assign score values for like samples on this basis. It became apparent that the

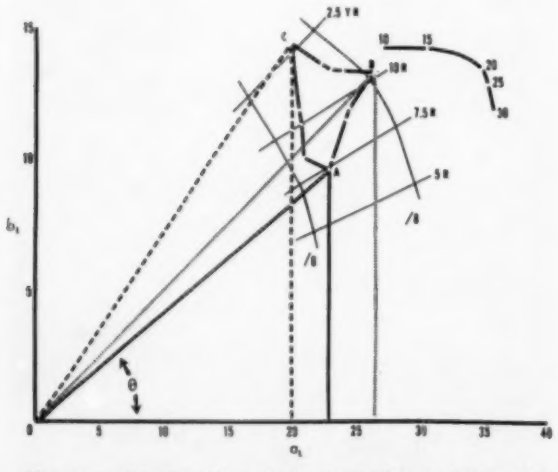

Figure 2. Representation of the array of raw tomato juice samples in Experiment 4 as a triangle ACB in Hunter-Munsell color space. Designated hue and chroma lines, as well as samples, are plotted at Munsell value 3 level.

TABLE 2

Hunter tristimulus values and visual scores for samples in Experiment 4, 1958

Sample	L	a_L	b_L	a_L/b_L	Visual score
1	21.9	22.8	9.5	2.39	27
2	23.0	20.8	9.8	2.13	22
3	24.5	20.8	11.3	1.84	18
4	25.3	20.4	11.9	1.72	16
5	28.3	19.9	14.4	1.39	8
6	27.5	21.9	13.6	1.61	13
7	27.4	22.8	13.4	1.71	13
8	27.2	23.7	13.1	1.82	14
9	27.0	26.3	13.3	1.97	15
10	24.8	24.4	11.9	2.05	18
11	24.4	24.2	11.5	2.11	19
12	23.2	22.9	9.7	2.36	24

observers were weighing their scores, in some way, by a more complete definition of the color of the samples than that afforded by Hunter L or a_L/b_L ratio alone. Only when the full significance of the positions of the samples in 3-dimensional color space was considered, did it become possible to arrive at an improved relationship.

Various manipulations of the color attributes defined by Hunter L, a_L and b_L were then tried in an attempt to combine them in an appropriate relationship that would give the highest correlation with visual evaluation. Of the numerous combinations attempted the ratio $\frac{a_L}{L}$ was the most fruitful. As noted in Table 3 and Figure 2, this ratio served to differentiate among scores alongside AC fairly well, side CB less well, whereas the large differences in scores alongside BA were not adequately accounted for by the $\frac{a_L}{L}$ ratio.

The a_L/b_L ratios for samples along this side BA were again reviewed (Table 3). The progression of this ratio was seen to account partially for the large differences in scores but not adequately. A further study of the trigonometric positions of the samples on this triangle then indicated that their distance from the origin of the a_L and b_L ordinates might serve as an index of differentiation. This distance $(a_L^2 + b_L^2)^{1/2}$ is the Index of Saturation frequently used in color technology *(7)*. By inserting the reciprocal of this Index, the formula $\frac{a_L}{L} \times \frac{1}{(a_L^2 + b_L^2)^{1/2}}$ was derived.

TABLE 3

Relative changes in color dimensions of samples in Hunter-Munsell color space [1]

Triangle position	a_L/L	Visual score	L	a_L	b_L	a_L/b_L	$(a_L^2 + b_L^2)^{1/2}$	$\frac{2000 \cos \theta}{L}$
Side AC	1.04	27	21.9	22.8	9.5	2.39	24.5	84.2
	.90	22	23.0	20.8	9.8	2.13	23.0	78.7
	.85	18	24.5	20.8	11.3	1.84	23.6	71.8
	.81	16	25.3	20.4	11.9	1.72	23.6	68.4
	.70	8	28.3	19.9	14.4	1.39	24.5	57.4
Side CB	.70	8	28.3	19.9	14.4	1.39	24.5	57.4
	.79	13	27.5	21.9	13.6	1.61	25.8	62.0
	.83	13	27.4	22.8	13.4	1.71	26.4	63.1
	.87	14	27.2	23.7	13.1	1.82	27.1	64.6
	.97	15	27.0	26.3	13.3	1.97	29.4	66.1
Side BA	.97	15	27.0	26.3	13.3	1.97	29.4	66.1
	.98	18	24.8	24.4	11.9	2.05	27.1	72.4
	.99	19	24.4	24.2	11.5	2.11	26.8	74.2
	.99	24	23.2	22.9	9.7	2.36	24.8	79.4
	1.04	27	21.9	22.8	9.5	2.39	24.5	84.2

[1] See Figure 2 for graphic representation.

This formula was then applied to all 58 samples of the 1958 studies and the correlation coefficient between the average of the visual scores and the formula was 0.97; the correlation of visual scores with Hunter L and a_L/b_L ratios was −0.93 and 0.94, respectively. Thus, the use of the combined formula was seen to result in substantial improvement.

The above empirical formula was simplified to $\frac{\cos \theta}{L}$, where $\cos \theta$ equals $\frac{a_L}{(a_L^2 + b_L^2)^{1/2}}$ and θ is the included angle in the a_L and b_L plot for a specific sample (figure 2). Multiplication of this formula by 2000 brings the values into a more desirable range for an index (from 57.4 to 84.2 for the samples in Table 3). This combined formula $\frac{2000 \cos \theta}{L}$ was then designated the T.C. (tomato color) index.

This work was repeated in 1959 with another group of trained observers. The calculation of correlation coefficients for the individual visual scores of all observers' versus Hunter L, a_L/b_L and T.C., substantiated the findings in 1958 (Table 4).

An algebraic identity of the formula $\text{T.C.} = \frac{2000 \cos \theta}{L}$ may also be expressed in terms of C.I.E. trichromatic coefficients as follows:

$$\text{T.C.} = \frac{21.6}{Y_c^{1/2}} - \frac{3.0}{Y_c^{1/2}} \left[\frac{Y_c - Z_c}{X_c - Y_c} \right],$$

where X_c, Y_c and Z_c are the usual trichromatic reflectance values for illuminant C. This formula was found to provide a more practicable basis for development of a new instrument to compute the T.C. index than $\frac{2000 \cos \theta}{L}$.

As the result of this research, an instrument was developed to measure raw tomato juice color by tristimulus colorimetry and automatically compute this index by appropriate analog circuitry. This instrument was used in the 1959 experiments. This new instrument called the Tomato Colorimeter was designed to be rugged and simple to operate. It is to be used to measure objectively, the color factor in the demonstration of a new modified inspection procedure for raw tomatoes for processing (Figure 3).

TABLE 4

Comparison of the coefficients of correlation (r) for the visual scores of various observers with instrument readings, 1958–1959 [1]

Observer	Reproducibility [2]	Hunter L [3]	Hunter a_L/b_L [3]	$\frac{2000 \cos \theta}{L}$ [3]
1958				
T. T.	0.95	−0.92	0.94	0.95
J. W.	.94	−.84	.90	.92
A. S.	.94	−.91	.92	.95
H. W.	.87	−.87	.91	.91
D. B.	.92	−.94	.86	.95
1959				
K. N.	.96	−.83	.92	.94
E. B.	.95	−.91	.92	.94
G. B.	.93	−.90	.89	.94
P. M.	.90	−.87	.91	.92

[1] The correlation coefficients reported in this table were obtained treating each observation individually.

[2] "r" of comparison between visual scores assigned to duplicate samples, n = 20; n = ca. 80 in 1958 and 1959, respectively.

[3] n = 40, in 1958; n variable in 1959 but >157 in all cases.

SUMMARY

The derivation of a new formula for computing raw tomato juice color from objective color measurement is described.

Carefully prepared Munsell disks having regularly spaced color attributes of hue, lightness and saturation in the region of raw tomato juice colors were used by trained observers as guides in visual scoring of the samples.

Visual color scores and instrument evaluations were determined for juice samples covering a wide gamut of color in Hunter-Munsell color space. Only when the 3-dimensional positions of the color readings of the juice samples in this system were visualized in relationship to the color scores, did it become possible to derive the formula which would best relate instrument evaluations with visual color scores.

The empirical formula $\frac{2000 \cos \theta}{L}$, named the T.C. index, computed from objective color measurement of

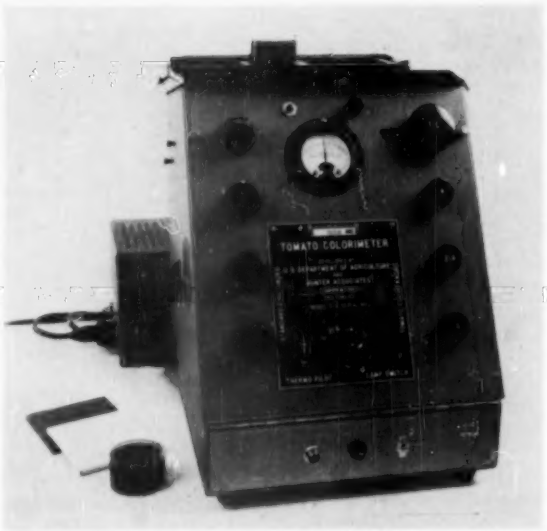

Figure 3. Tomato Colorimeter (developed by U. S. Department of Agriculture and Hunter Associates, Incorporated, McLean, Virginia).

a wide gamut of samples in the region of tomato color in Hunter-Munsell color space, was found to weight appropriately the Hunter color values to correlate best with visual scores assigned by trained observers.

A rugged tristimulus photoelectric instrument has been constructed to measure the designated T.C. index.

Acknowledgment

The authors wish to acknowledge the valuable assistance provided by personnel of the Fruit and Vegetable Division, Agricultural Marketing Service, who served as trained observers in these studies. Also, we wish to thank the Macbeth Daylighting Corporation for supplying standardized daylight filters and light sources for the disk colorimeters and the Munsell Color Company for providing C.I.E. specifications of the Munsell papers used in the disks.

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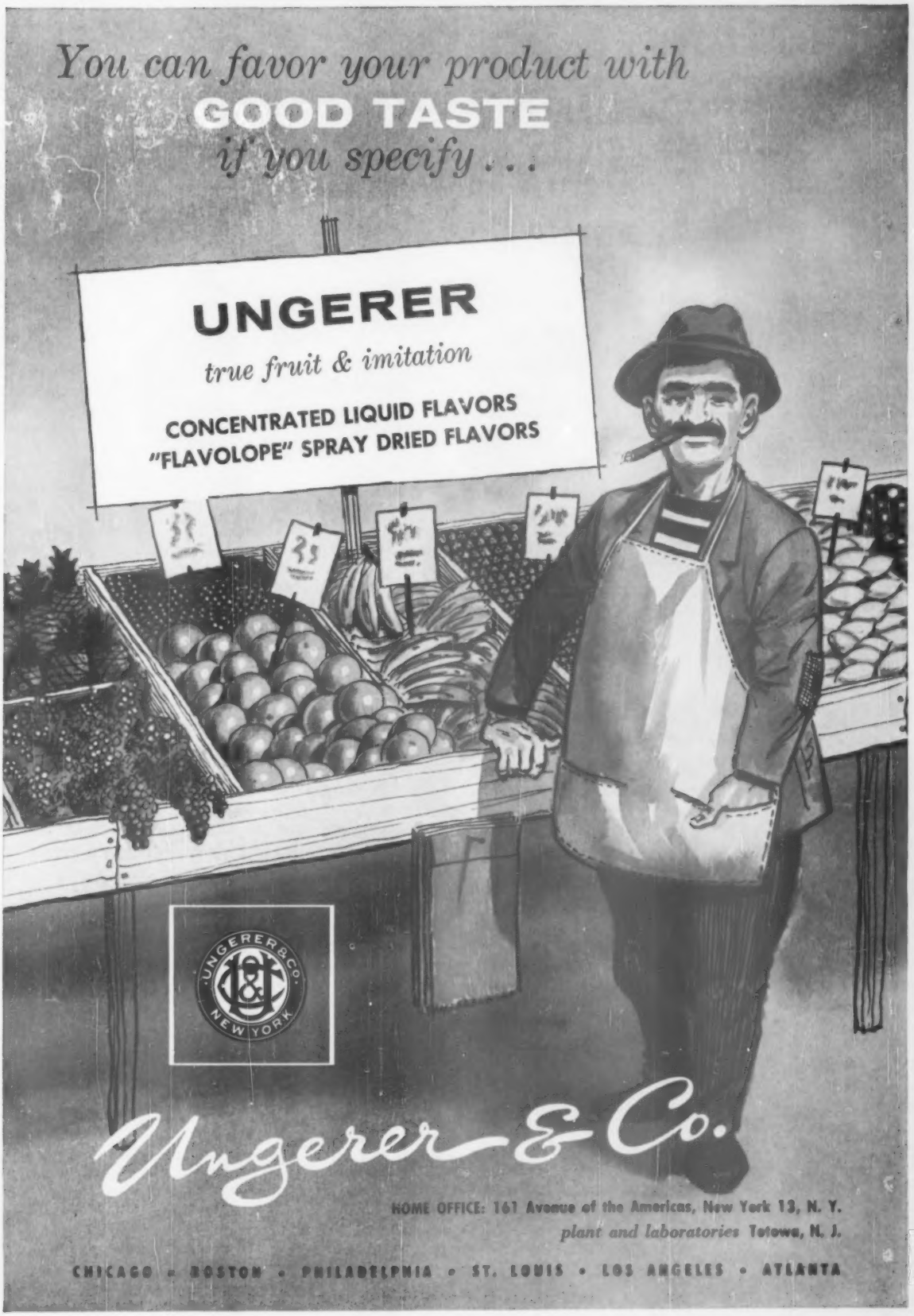
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Microorganisms Associated with Spoilage of Refrigerated Poultry[a]

(Manuscript received June 26, 1959)

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STUDIES BY AYRES *et al. (1)* strongly implicated bacteria of the genus *Pseudomonas* as the chief cause of spoilage of chilled, eviscerated poultry meat. Since that time several changes have taken place in the processing and marketing of poultry. For example, now it is much more common to eviscerate the birds immediately after slaughter and defeathering. In addition, chickens are being processed in widely different parts of the country and shipped in chipped ice long distances to market. Also the antibiotics, chlortetracycline and oxytetracycline, frequently are used in the ice slush used for chilling the freshly dressed birds. Finally, cutting-up operations are heavily concentrated in the retail markets instead of in the processing plants.

Some changes have been made during the past few years in the taxonomic scheme for classification of bacteria *(3)*. These might conceivably affect the distribution of genera to which the spoilage organisms would be assigned. Also Shewan *et al. (7)* reported that oxytetracycline inhibited the growth of non-pigmented *Pseudomonas* organisms, but not the pigmented species. This observation suggests that antibiotic sensitivity might be used as an additional criterion for more precise classification of these organisms. It also implies that the pigmented *Pseudomonas* species would be the ones causing spoilage of birds treated with the tetracyclines.

The present investigation was undertaken to determine the types of bacteria associated with the spoilage of chilled poultry under present conditions of processing and marketing, as well as the possible influence of geographical location of processing facilities, location of cutting-up operations, and the use of antibiotics.

EXPERIMENTAL METHODS

Cultures were isolated from cut-up, tray-packed fryers purchased in retail markets in the Sacramento, California area. The birds were deliberately stored for seven days (from the date of purchase) at 4.4° C. (40° F.) before sampling. This combination of time and temperature had been found to be sufficient to result in typical spoilage. Eugonagar plates streaked from dilutions of swab samples taken from the birds were incubated at 4.4° C. (40° F.) for 7 days. Isolations were made from the predominant colony type obtained after restreaking twice on Eugonagar. These isolates were then maintained on nutrient agar slants also kept at 4.4° C. (40° F.).

Morphology, motility and flagellation. Observations for motility and cell morphology were made with the phase microscope using wet mounts prepared from growth on moist nutrient agar slants incubated at 20° C. (68° F.) for 12–24 hours. All cultures were stained for flagella by the method of Leifson *(6)*. Cell morphology also was observed on Gram-stained preparations.

Diffusible pigments. Giant colonies, grown on medium B of King *et al. (5)*, incubated at 20° C. (68° F.) were observed daily over a seven-day period for production of diffusible pigments.

Growth at 37° C. (98.6° F.). The appearance of turbidity within two days in inoculated tubes of nutrient broth was considered as positive for growth of cultures at this temperature.

Biochemical reactions. The isolates were differentiated further on the basis of their activity in litmus milk, glucose broth, and on gelatin stabs. The gelatin tubes were incubated at 20° C. (68° F.) and observed up to 35 days for evidence of liquefaction. The glucose and litmus milk tubes were incubated at room temperature. Brom-cresol purple (0.04% w/v) was added to the glucose medium as an acid indicator. Unless otherwise indicated, the procedures used for these tests were those found in the *Manual of Microbiological Methods (9)*.

Sensitivity to antibiotics. Sensitivity to penicillin and oxytetracycline was determined by the pad-plate technique. Two hundredths of a ml. of an aqueous solution containing the desired concentration of penicillin G[b] or oxytetracycline[c] was added to a 12.7 mm. sterile pad. Otherwise, the tests were performed as described by Shewan *et al. (7)*.

RESULTS AND DISCUSSION

Two morphological types predominated among the 103 cultures isolated. The first group of 90 isolates, typical of the genus *Pseudomonas*, ranged from coccoid through medium to long rods. Their cells usually occurred singly or in pairs. The variation in morphology within a given isolate was often so great as to suggest a mixture rather than a pure type. However, extensive replating established that such variable cell morphology was normal for the isolates in question.

Eighty-six of the cultures were motile rods, all of which were polarly flagellated. One of these motile types produced acid and gas from glucose but did not ferment lactose. This latter culture was allocated to the genus *Aeromonas*. The remaining 85 cultures were classified as typical members of the genus *Pseudomonas*.

[a] Presented at the Nineteenth Annual Meeting of the Institute of Food Technologists, May 19, 1959, Philadelphia, Pennsylvania.

[b] E. R. Squibb & Sons.

[c] Chas. Pfizer & Co., Inc.

TABLE 1

Some characteristics of the cultures isolated from spoiled poultry meat

Genus	Total No.	Motility		Growth at 37° C.		Glucose				Gelatin liquefaction		Fluorescent pigment	
						Acid		Gas					
		No. +	% +	No. +	% +	No. +	% +	No. +	% +	No. +	% +	No. +	% +
Pseudomonas	88	85	97	1	1	79	90	0	0	67	76	13	15
Aeromonas	2	1	50	2	100	2	100	2	100	2	100	0	0
Achromobacter-Alcaligenes	13	0	0	1	8	1	8	0	0	0	0	0	0
Totals	103	86	84	4	4	82	80	2	2	69	67	13	13

TABLE 2

Sensitivity of spoilage organisms to oxytetracycline and penicillin

Genus	Total isolates	Terramycin 10γ		Penicillin			
				5 units		10 units	
		No.[1]	%[2]	No.[1]	%[2]	No.[1]	%[2]
Non-pigmented *Pseudomonas*	75	46	61	0	0	2	3
Fluorescent *Pseudomonas*	13	7	54	0	0	0	0
Aeromonas	2	0	0	0	0	0	0
Achromobacter-Alcaligenes	13	4	31	8	62	11	85
Totals	103	57	55	8	8	13	13

[1] Number of isolates sensitive to the antibiotic.
[2] Per cent of isolates sensitive to the antibiotic.

On the basis of morphology, resistance to penicillin, acid production from glucose and development of fluorescent pigment, three of the non-motile cultures were also classified as members of the genus *Pseudomonas*. The other non-motile culture produced acid and gas from glucose but not from lactose and was insensitive to penicillin and terramycin. This latter organism might have been classified either as an *Aeromonas* or as a member of the *Enterobacteriaceae*. The present authors chose to call it an *Aeromonas* type because of its similarity to the motile *Aeromonas* described above.

The other morphological type (13 cultures) was characterized as Gram-variable, short, plump rods occurring singly, in pairs or chains. This morphological group always was non-motile and was easily differentiated from the *Pseudomonas* cultures. These cultures biochemically were relatively inactive. They did not liquefy gelatin and 12 of the 13 did not produce acid from glucose but instead only produced islets or a ring of growth on the surface of the medium. Litmus milk was turned slightly acid by nine of these cultures whereas the remaining four isolates produced an alkaline reaction. Without question these organisms belong to either the genus *Achromobacter* or the genus *Alcaligenes*, so they will be referred to as the *Achromobacter-Alcaligenes* group in the following discussion.

Table 1 summarizes some of the morphological and biochemical characteristics of the spoilage organisms investigated in the present study. These taxonomic results corroborate and extend those of Ayres *et al. (1)*. It is evident that the *Pseudomonas* species are the most common type of bacteria associated with the spoilage of chilled, eviscerated chicken. *Aeromonas* and members of the *Achromobacter-Alcaligenes* group represent only a minor portion of the bacteria present at time of spoilage of properly chilled poultry meat.

The results on sensitivity of the cultures to terramycin and penicillin are given in Table 2. It was necessary to use a concentration of 10 units of penicillin to inhibit most of the organisms in the *Achromobacter-Alcaligenes* group. In contrast only two of the *Pseudomonas* and none of the *Aeromonas* cultures were sensitive to 10 units of penicillin. Peculiarly enough, a fair proportion of both the non-pigmented and fluorescent *Pseudomonas* isolates were sensitive to 10 γ of oxytetracycline. These results are not consistent with those reported by Shewan *et al. (7)* who differentiated the pigmented from the non-pigmented *Pseudomonas* species on the basis of their sensitivity to this antibiotic. These workers also claimed that *Achromobacter* species were sensitive to oxytetracycline. However, only a portion of the cultures of this latter group investigated in the present study were sensitive.

Table 3 shows the distribution of genera according to whether the birds had been processed in California or elsewhere. No significant differences were noted. Of the 33 birds processed in other states, 19 came from Alabama, 9 from Georgia, 3 from Arkansas and one each from Louisiana and Mississippi.

TABLE 3

Generic distribution of cultures isolated from spoiled poultry

Genus	From California		From other states	
	No.	%	No.	%
Pseudomonas	62	89	26	79
Aeromonas	1	1	1	3
Achromobacter-Alcaligenes group	7	10	6	18
Totals	70	100	33	100

The influence of antibiotic treatment (according to label declaration) on the distribution of genera of spoilage organisms is shown in Table 4. No significant differences were found. This observation corroborates those of Ayres *et al. (2)* and Simpson *et al. (8)*.

TABLE 4

Generic distribution of cultures from spoiled, antibiotic treated and untreated poultry

Genus	Untreated		Treated	
	No.	%	No.	%
Pseudomonas	67	86	21	84
Aeromonas	1	1	1	4
Achromobacter-Alcaligenes	10	13	3	12
Totals	78	100	25	100

TABLE 5

Generic distribution of cultures from store and processing plant wrapped poultry

Genus	Processing plant		Store	
	No.	%	No.	%
Pseudomonas	29	88	59	84
Aeromonas	0	0	2	3
Achromobacter-Alcaligenes	4	12	9	13
Totals	33	100	70	100

Table 5 presents the data on distribution of genera as affected by location of the cutting-up operation. Again no significant differences were noted.

The possibility existed that the types of bacteria recovered from the spoiled birds might have been influenced by the rather variable time between slaughter and sampling for it is conceivable that organisms actually responsible for spoilage of the poultry meat could have been overgrown by other microorganisms. However, as shown in Table 6, the distribution of

TABLE 6

Generic distribution of cultures as related to days elapsed between slaughter and purchase of poultry

Genus	Number of days between slaughter and purchase (range)[1]		
	1–3	4–6	7–14
	Number of cultures		
Pseudomonas	32	31	27
Aeromonas	1	0	1
Achromobacter-Alcaligenes	3	3	4

[1] After purchase all birds were stored for 7 days at 40° F. (4.4° C.).

kinds of spoilage organisms was remarkably similar regardless of the number of days between slaughter and purchase of the birds. Since the laboratory incubation time and temperature were constant (7 days at 40° F., 4.4° C.) and the birds presumably were not spoiled at time of purchase it would seem logical to believe that the genera encountered here are the most important ones to be associated with spoilage of refrigerated poultry meat.

The isolation of *Aeromonas* species is of interest since these organisms are facultative anaerobes. [This genus has already been reported to occur on refrigerated beef by Brown & Weidemann *(4)*]. Thus they could be expected to be important in spoilage where oxygen impervious packaging material is being used. One such packaging material (Cryovac) is available but is seldom used for chilled poultry. It would be interesting to see whether the species would actually assume a major role in the spoilage of poultry packed in this material.

SUMMARY

One hundred and three cultures were isolated from chilled, cut-up fryers which had been allowed to spoil at 4.4° C. (40° F.). Eighty-eight of the cultures were allocated to the genus *Pseudomonas*. Two additional cultures were classified as members of the genus *Aeromonas*. The remaining thirteen cultures were assigned to the *Achromobacter-Alcaligenes* group without any attempt being made to place them specifically in either genus.

The use of oxytetracycline as an aid in more precise classification of the *Pseudomonas* species from spoiled poultry was found to be of little value. Penicillin sensitivity also was not completely reliable for differentiation between the *Achromobacter-Alcaligenes* group and members of the genus *Pseudomonas*.

The geographical location of processing facilities, location of cutting-up operations, and the use of antibiotics had no influence on the distribution of genera of spoilage organisms investigated in this study.

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Radiation Preservation of Milk. X.

Studies on the Radiation Induced Gelation of Concentrated Milk. Methods, and Effect of Some Additives[a, b]

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(Manuscript received May 21, 1959)

WHEN MILK IS EXPOSED to ionizing energy it undergoes changes which have been previously described *(1, 2, 8)*.

Storage studies *(2)* have shown that concentrated, irradiated milk stored at room temperature or higher has a marked tendency to gel. In milk of normal concentration, or in concentrated milk stored under refrigeration, gelation is not as apparent. Preliminary studies have indicated that the addition of different inorganic salts to milk had a noticeable effect on the "gelling time" of milk in storage. It was, therefore, believed that a systematic study of such additives might yield information leading to a reduction or elimination of the problem of gelation. It would also be of interest to find out whether the gelation of irradiated milk bears any relation to the gelation phenomena observed in heat-processed milk.

This paper describes the methods used in the study of the radiation induced gelation and the effect of some additives.

EXPERIMENTAL

Milk. Commercial grade A pasteurized and homogenized milk was concentrated under reduced pressure (temperature 30° C.) to a final concentration of approximately 36% total solids content, concentrated 3:1. The concentrated milk was kept at refrigeration temperature (5° C.) when not utilized immediately.

Radiation source. A General Electric 1 MEV Resonant Transformer was used as the radiation source. All the samples were given a dose of 2 megarad, which was sufficient to completely sterilize the milk.

Irradiation and storage of samples. The utilizable penetration of 1000 KVP electrons produced by the Resonant Transformer in milk is only about 2.5 mm. Since this penetration restricts the physical shape of samples to be irradiated, as well as the amount of sample available for the estimation of gel strength, a special technique had to be developed. The adopted technique required only a limited amount of milk for each determination of gel strength and yet was reproducible to the extent of rendering comparative studies possible.

Melting point capillary tubes (Kimax brand), 10 cm. long, were filled with sufficient milk to give a milk column 4 cm. long. The ends of the filled tubes were covered with a small amount of cotton. The tubes were put into individual polyethylene bags that were heat-sealed and then irradiated in a horizontal position on the conveyor belt transversing the electron beam. The irradiated tubes were stored at 37° C. in an atmosphere saturated with water vapor (Figure 1). The temperature of 37° C. was chosen in order to give a relatively rapid gel development. Results obtained at 37° C. could be correlated with those at lower temperatures *(2)*.

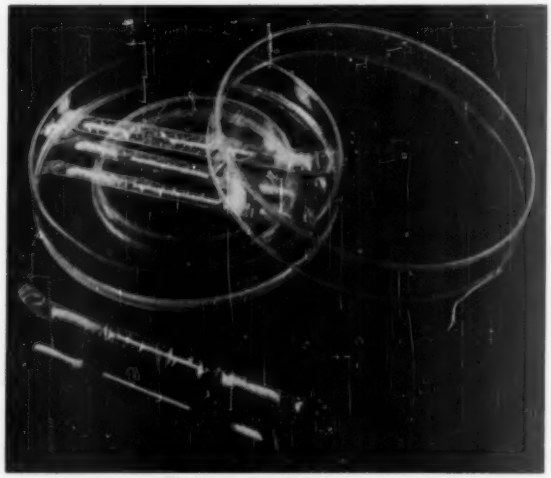

Figure 1. Irradiated tubes.

Estimation of gel strength. The samples were inspected periodically for presence of flow when put in a slanting position, and, if they appeared to be gelled (no flow), the gel strength was estimated by recording the gas pressure needed to break the gel, thereby forcing the gelled milk out of the capillary tube. Satisfactory reproducibility was obtained for the first part of the curve of gel strength as a function of storage time (in which gel strength is increasing), provided that the outside diameter of the tubes was uniform within ±.0125 mm.

Heat treatment of irradiated milk. It was observed at the outset of this investigation that irradiated concentrated milk gels when heated in a boiling water bath. It seemed to be of interest to investigate whether the heat-induced gelation of irradiated milk would respond to the additives in a similar way as the gelation observed when irradiated milk is stored for a length of time.

The milk was therefore heated in open capillary tubes without cotton plugs at 90° C. At this temperature the rate of gelation is sufficiently rapid to prevent drying out. At temperatures closer to the boiling point there is a danger of gel disruption by the development of gas bubbles. A stable temperature of 90° C. was obtained by boiling an azeotropic mixture of isobutanol and water in a copper container as illustrated in Figure 2. The tubes are heated in an air chamber which is completely surrounded by the boiling liquid. Two small water baths and a hinged door tend to prevent evaporation of water from the exposed surfaces of the milk. Gel strength was estimated in the same way as for the stored samples. Satisfactory reproducibility was obtained when the heated samples were cooled to 0° C. for 30 minutes before making measurements of the gas pressure required to break the gel.

Additives. Analytical grade chemicals were used throughout. Additions were made, before irradiation, from relatively concentrated aqueous stock solutions of the particular additives. All the samples in one series were adjusted to the same total solids content by the addition of water. The metal ions were

[a] Contribution No. 369 from the Department of Food Technology.

[b] Presented at the Nineteenth Annual Meeting of the Institute of Food Technologists, May 19, 1959, Philadelphia, Pennsylvania.

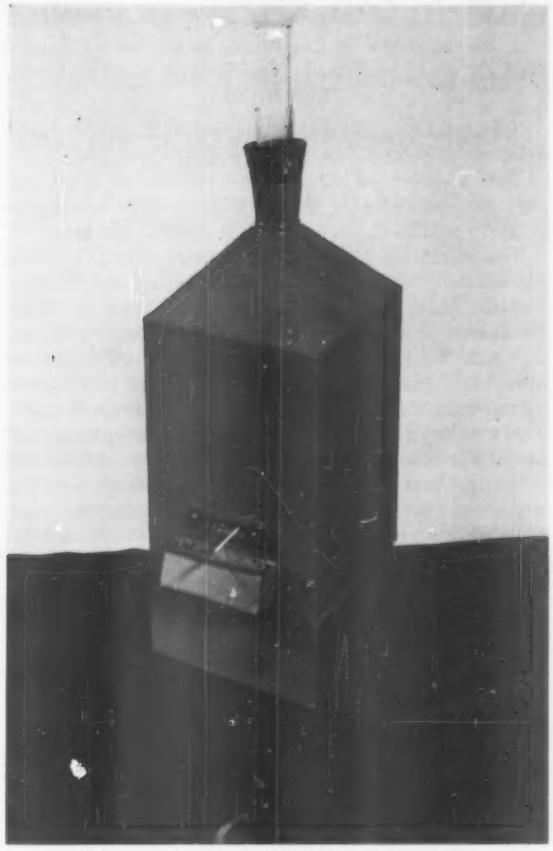

Figure 2. Copper containers for heating tubes.

added as chlorides. The concentrations of added ions are in Figures 3, 4 and 5 expressed as milliequivalents per liter of concentrated milk.

RESULTS AND DISCUSSION

The answers to two questions were sought in this investigation. The first was concerned with the effect of additives on the radiation-induced gelation and the possibility of delaying or preventing the occurrence of the gelation in storage. The second question was concerned with the relation, if any, of the radiation-induced gelation to the gelation phenomena observed in heat processed milk.

The effect of addition of varying quantities of sodium diphosphate and sodium citrate on the development of gel in irradiated milk on storage is illustrated in Figure 3. These additives appear to enhance the rate of gel formation and also cause an increase in the gel strength.

The gel strength, as a function of time, tends to approach a maximum, after which the gel strength readings tend to become erratic. Only the first portion of the curve could therefore be presented graphically. The maxima are probably connected with the onset of syneresis and flocculation.

The effect of the addition of several metal salts on the development of gel strength as a function of time

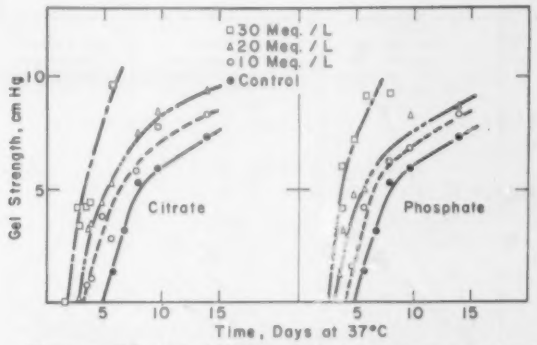

Figure 3. Effect of additives on gelations in storage of irradiated milk.

of storage at 37° C. is shown in Figure 4. Calcium ions at the concentrations used do not significantly affect gel formation. The effect of magnesium ions is pronounced and at low concentrations significantly increases gelling time and reduces gel strength. The effect of manganese ions is even more pronounced and, at a concentration of 20 milliequivalents per liter of concentrated milk, completely prevented gel formation with no indication of viscosity changes for the duration of the experiment (60 days). As no gel was formed, these observations do not appear in Figure 4.

The effects noted in Figures 3 and 4 are contrary to the effects of these additives in the most common cases of normally processed heat-treated (240° F. for 20 minutes) concentrated milk (unirradiated). It is well known [see for instance *(4)*] that such milks tend to gel and that citrate or phosphate is added in most cases in order to delay this development, while the addition of Ca^{++} has an adverse effect. The effects of these additives in irradiated milks, which have been brought to gel by a heat treatment at 90° C., seem to parallel the effects just mentioned. The gel formation is affected by the addition of citrate and phosphate to yield a reduced rate of gel strength development (Figure 5). Addition of calcium causes, on the other hand, a marked increase of this rate. No significant effect on the gelling time was found.

Unirradiated milk does not gel under these conditions even after prolonged heating periods.

The experimental results suggest that the mechanisms underlying the two phenomena are different. The irradiation has, in some unknown manner, disturbed the inherent stability of the casein micelles.

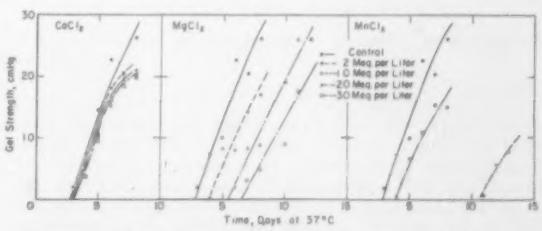

Figure 4. Effect of metal salts on gelation in storage of irradiated milk.

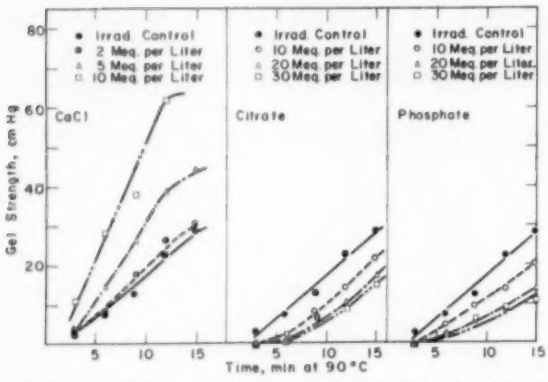

Figure 5. Effect of additives on heat induced gelation of irradiated milk.

The lability produced is then manifested in different ways, depending on the further treatment given to the milk. Heat may cause a massive disruption of hydrogen bonds resulting in the collapse of the structure of the micelle system and produces a gross coagulation of protein. This development is not appreciably affected by additives, that is, it is mostly dependent on the energy input. The resulting gel structure, however, may be somewhat influenced by such additives. Storage gelation seems, on the other hand, to come about through a disturbance of the electrostatic balance of the micellar system that has occurred due to irradiation, and is easily influenced by changes in the ionic composition of the milk.

The sites at which the disturbances have occurred are seemingly restricted sterically to the approach of cations such as Ca^{++} while permitting the interaction with other cations such as Mg^{++} and Mn^{++}. It is suggested that these sites could be pyro-phosphate linkages essential for the stabilization of the casein micelles. Such linkages would be expected to react preferentially when subject to ionizing radiations. It is also known *(7)* that compounds of this nature form complexes preferentially with certain cations depending on the ionic radii and on the coordination numbers of the ions. The existence of pyro-phosphate linkages in casein has been demonstrated by Perlmann *(5)*, although her findings have lately been disputed *(3, 6)*.

SUMMARY

A method was devised whereby irradiation induced gelation of concentrated milk could be studied.

The addition of 20 milliequivalents of Mn^{++} per liter of concentrated milk (3:1) totally prevented gelation within the experimental period (60 days).

The formation of a gel during storage at 37° C. was considerably delayed by the addition of the divalent cations, Mg^{++} and Mn^{++}, whereas Ca^{++} had no effect. Phosphate and citrate were found to enhance gelation.

When the gelation of the irradiated milk was induced by heating at 90° C., Ca^{++} addition effected an increase in gel strength, whereas citrate and phosphate reduced the gel strength. No significant change in gelling time was observed under these conditions.

On the basis of the experimental observations it is suggested that irradiation causes the rupture of pyrophosphate linkages essential to the stability of the casein micelles.

Acknowledgment

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Radiation Preservation of Milk. XI.

Studies on the Radiation-Induced Gelation of Concentrated Milk. The Effect of Polyphosphates[a, b]

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(Manuscript received May 21, 1959)

THE RADIATION-INDUCED GELATION of concentrated milk has been the subject of study of two earlier papers of this series *(2, 3)*. At a fixed dose of approximately 2 megarads, a dose established as the sterilization dose for raw whole milk, the gelation was observed to be affected only by the concentration of the milk and by the storage temperature, whereas various processing variables such as dose rate, temperature of irradiation and distillation, were found to have no effect.

When the effect of additives was studied, it was observed that citrate and phosphate ions both, enhanced the gelation, whereas $CaCl_2$ had no effect on the amounts added. On the other hand, $MgCl_2$, and especially $MnCl_2$, were found to exhibit a pronounced effect in delaying the development of a gel. Similar studies of irradiated milk that had been subsequently heat-treated, revealed that the irradiation had sensitized the milk towards this treatment, and that the effects of additives were different from the effects observed during storage, and similar to effects known to occur with normal non-irradiated heat-sterilized evaporated milk (240° F. for 20 minutes).

It was of interest to investigate other means of preventing gel formation. The addition of polyphosphates was suggested since these compounds have the ability to chelate metallic ions and interact strongly with proteins. Analysis of the ionic compositions of ultrafiltrates was included in this investigation as it seemed reasonable to expect that the effects of irradiation would be reflected in changes in their composition.

EXPERIMENTAL

Method for the evaluation of gelation. The samples were prepared, stored and tested for gel strength in a manner identical to that described previously *(2)*. Melting point capillary tubes were filled with approximately 3:1 concentrated milk containing the additives. The filled tubes were heat sealed in polyethylene bags, irradiated with a dose of 2 megarads and stored at high humidity at 37° C. The observation that no flow occurred when the tubes were put in a slanting position was used as criterion of gelation, and the elapsed time in storage when this occurred was denoted "gelling time." Gel strength was estimated by noting the gas pressure needed to break the gel or force the milk out of the tubes.

Additives. The additives used were: sodium tripolyphosphate (Monsanto Chemical Co.) of approximately 96% purity, adenosine triphosphate (ATP) of approximately 98% purity (Sigma Chemical Co.) and "hexametaphosphate" (Quadrafos, Rumford Chemical Works). This particular sample appeared to consist of a complex mixture of pyro-, tripoly, tetrapoly, and higher polyphosphates when evaluated by paper chromatography.

Ultrafiltration. Ultrafiltrates of milk were obtained according to a method given by Tessier and Rose *(6)*. Ten ml. was collected from 100 ml. milk using a gas pressure of 30 p.s.i.g.

Determination of calcium and magnesium. The method of Jenness *(4)* was followed.

Determination of inorganic orthophosphate and total phosphate. These were obtained using a modification of the Fiske-SubbaRow method *(1)*.

RESULTS

Orthophosphate, in the form of sodium diphosphate was found *(2)* to shorten gelling time and to increase the gel strength, but different results are obtained with polyphosphates (Figure 1). Pyrophosphate extends gelling time and

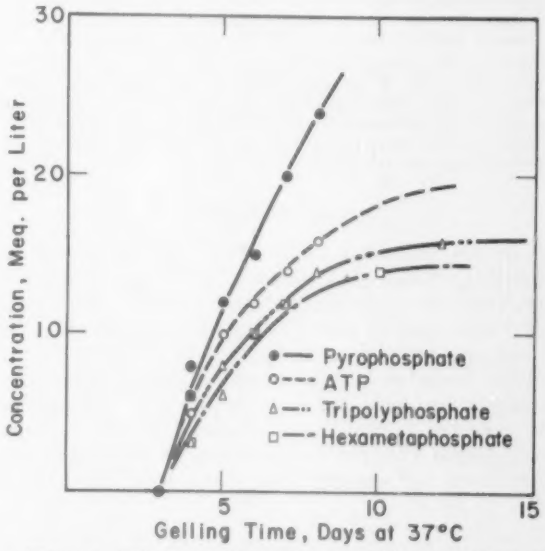


Figure 1. Effect of polyphosphate on gelling on storage of irradiated milk.

reduces the gel strength, but it does not, at the concentrations used here, prevent the eventual formation of a gel. The next higher member in the series of polyphosphate homologues—tripolyphosphate—was found to completely prevent gel formation during a storage period at 37° C. of approximately 60 days, when added in amounts larger than 16 milliequivalents per liter of concentrated milk. (A storage time in excess of 2 months was usually not possible. The polyethylene bags even-

[a] Contribution No. 370 from the Department of Food Technology.

[b] Presented at the Nineteenth Annual Meeting of the Institute of Food Technologists, May 19, 1959, Philadelphia, Pennsylvania.

tually, after this period of time, succumb to an invasion of mold.)

Adenosine triphosphate (ATP), which may be considered as a tripolyphosphate with one end-group esterified, produces an effect which falls between the effects of pyrophosphate and tripolyphosphate. Tripolyphospate and "hexametaphosphate" appear to give very similar effects when compared on an equivalent basis. (Hexametaphosphate taken as 100% tetrapolyphosphate.) A threshold value seems to exist for polyphosphate additives that contain more than two phosphorus atoms per molecule. Below this value the additive has only slight effect on the gelling time. At the threshold value there is an abrupt change in the gelling time and a point is reached where what appears to be total prevention of gel formation is obtained.

Table 1 gives the chemical analysis of the ultrafiltrates. The amount of tripolyphosphate used in these experiments was in slight excess of the threshold value: 16 milli-equivalents per liter or 300 mg. P per liter.

It is observed that the irradiation of concentrated milk results in an increase in the free metal ion concentration. The increase is relatively greater for Mg^{++} than for Ca^{++}. The addition of tripolyphosphate results in increased binding of metal to the proteins as judged by the reduced levels of these metals found in the ultrafiltrates. Relatively more Mg^{++} than Ca^{++} is bound. The irradiation of milk with added tripolyphosphate gives little change in the free metal ion concentration, the Mg^{++} concentration being, in this case, totally unaffected.

The changes observed are relatively small, but the same trend of changes has been noted repeatedly. It is considered, therefore, that the statements above concerning qualitative changes are correct, whereas conclusions derived from the magnitude of changes as given in Table 1 would be less reliable.

Further inspection of Table 1 shows that irradiation causes an increase in the total phosphate of the ultrafiltrate, the increase being approximately equally shared by the inorganic orthophosphate and other phosphates (organic and polyphosphates) present. The addition of tripolyphosphate does not significantly change this level of inorganic orthophosphate, but a slight increase in the total phosphate is observed. If it is assumed that this increase would be all tripolyphosphate, it is indicated that tripolyphosphate is strongly held by the protein, only about 10% of the amount added appearing in the ultrafiltrate. When milk containing tripolyphosphate is irradiated, a significant increase in the total phosphate occurs, all of which appears to be inorganic orthophosphate—perhaps produced by hydrolysis of the tripolyphosphate.

DISCUSSION

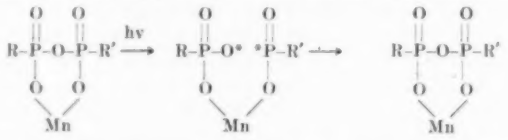
It was suggested earlier *(2)* that the radiation-induced gelation of concentrated milk might be caused by a rupture of pyrophosphate linkages of the casein. The hydrolysis of these linkages, if such occurs, could yield two orthophosphate groups of greatly reduced ability to chelate with metal ions as compared with the original structure. Such a reaction would, therefore, be expected to result in a release of metal ions from complexing with the casein, giving an increase in the free metal ion concentration of this milk. One would also expect an increase in the inorganic orthophosphate concentration, these ions being released from the secondary binding to the casein through the metal ions.

The hypothetical rupture of pyrophosphate linkages could further be expected to result in a loss of structure of the casein molecules. In the process of uncoiling in a random manner new ionic bonds and hydrogen bonds would be formed between adjacent molecules, and, as an end product, give a gel.

The experimental results tend to support this interpretation of the effect of irradiation. Both the concentrations of divalent cations and of free phosphate were found to increase as was expected. The relatively greater increase in Mg^{++} than of Ca^{++} further supports the rupture of pyrophosphate linkage, as Mg^{++} would be more strongly held by such groups than Ca^{++}.

The effect of added metal ions, which was reported in an earlier paper *(2)*, and of the polyphosphates as reported here, appears to be less easily explicable. The similarity of the effects of added manganese ions and of tripolyphosphate seems to preclude interpretations based upon classical colloidal chemistry ideas. It is not known whether one is dealing with "protection" effects or with "repair" effects of these additives. Based on the present information, some possible interpretations are presented in the following.

Manganese ions are known to possess a greater affinity for the type of phosphate linkages assumed to be involved *(5)*. Their presence could be thought of as either reinforcing this structure, rendering it less vulnerable to irradiation damage, or tending to recombine any momentarily broken O-P bond by giving extra rigidity to the structure in this manner:



The structure would actually be more rigid than expressed in this formulation, as the manganese complex is probably polydentate rather than bidentate as shown. Another alternative is:

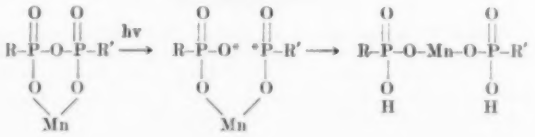


TABLE 1

Chemical analysis of the ultrafiltrates

Sample	Metal in ultrafiltrates		% change from untreated milk		Inorganic ortho-phosphate	Total P in UF	Organic + Poly-P
	Ca (mg./liter)	Mg (mg./liter)	Ca	Mg	mg./liter	mg./liter	mg./liter
Nonirradiation	639	138	0	0	760	900	140
Irradiation	659	145	+3	+9	800	990	190
Nonirradiation + TPP	582	123	−9	−11	750	930	180
Irradiation + TPP	598	123	−7	−11	830	1000	170

The amount of tripolyphosphate used in these experiments was in slight excess of the threshhold value: 16 milli-equivalents per liter or 300 mg. P per liter 3:1 conc. milk.

where manganese forms new ionic bonds between the products of hydrolysis. The stability of complexes of substituted orthophosphates with Mn^{++} is approximately eight times greater than that of such complexes involving Ca^{++} *(5)*.

The effect of polyphosphates could be interpreted in a very similar manner. These molecules might be thought of as arranging themselves along the surface of the micellar protein, as indicated by the complex formations discussed previously, thus strengthening the structure existing in the native protein. Obviously, both a protection effect as well as a repair effect would again be possible explanations.

Finally, the polyphosphates as complexed with protein, might act as "radical acceptors," reacting preferentially with free radicals produced during the irradiation and thus sparing the pyrophosphate linkage of the proteins.

Post-irradiation addition of the gel preventing compounds would undoubtedly clarify the mechanism to some extent and make possible the choice as to which of these interpretations, if any, is more likely to be the correct one.

SUMMARY

The addition of polyphosphates to concentrated (3:1) milk before irradiation markedly reduces the tendency of irradiated milk to develop a gel when stored at 37° C.

ATP, tripolyphosphate and "hexametaphosphate" were able to prevent gel formation for an undetermined length of time in excess of two months at 37° C. when added in amounts above a certain threshold value specific for each compound. Pyrophosphate did not exhibit this phenomenon.

The analysis of ultrafiltrates of irradiated milk demonstrated that the irradiation caused a release of Ca^{++}, Mg^{++} and phosphate ions from complexing with the casein. Addition of tripolyphosphate to irradiated milk caused an increased complexing of these ions with casein. Nearly all the added tripolyphosphate was found to complex with the protein.

Irradiation of milk with added tripolyphosphate did not affect the metal-protein complex, but did result in a release of inorganic orthophosphate and other phosphates from the casein complex.

The experimental results are discussed and an interpretation of the effects of irradiation and of the addition of metal ions and polyphosphate is attempted.

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Changes in Volatile Constituents During the Baking of Sherry Wine by the Tressler Process[a, b]

(Manuscript received May 21, 1959)

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THE MAJORITY of the sherry wine produced in New York State is made by the Tressler Baking Process. Introduced in 1938, the method has since been adopted as standard procedure by the wine industry in this State. The process is particularly adapted to use with Concord and other Labrusca-type grapes, since the strong "foxy" odor and bright red color, objectionable qualities in a sherry wine, are eliminated in a relatively short time *(1)*. Thus, an excellent quality sherry can be produced more quickly at less expense.

Heitz *et al. (2)* investigated the effect of certain factors which influenced the composition of California type sherry during the baking process. The baking process employed by these investigators differs from the Tressler process. Sherry wines prepared by the Tressler process are baked for a period of 6 weeks at 140° F. while the California process bakes sherry wine for 13 weeks at 120° F. The Tressler process employs a constant flow of oxygen during the baking process; Heitz *et al.* used intermittent aeration once a week for two minutes.

The Tressler process has had no major alterations since its conception. Very little is known about the changes that take place during this baking process. The development of new analytical techniques made possible an evaluation of the method from an objective viewpoint. Data are also needed to characterize the process in order to control and insure uniform quality.

This investigation was designed to permit study of the changes in the general classes of volatile components of sherry wine during the Tressler Baking Process. The volatile classes studied were the carbonyl, ester, and acid.

METHODS AND MATERIALS

Preparation of the wines. The wine samples obtained in this investigation were prepared in a commercial winery. They were baked at 140° F. with a constant flow of finely dispersed oxygen. Samples were taken at various time intervals throughout the baking process. Wines made from grapes of the Concord and Niagara varieties were employed in this investigation. No sulfur dioxide was used in the preparation of these wines.

Steam distillation of the volatiles. One hundred ml. of wine was steam distilled at the rate of 5 ml./min. The steam generator consisted of a 3-necked 500 ml. flask fitted with an internal coil of nicrome wire immersed in boiled distilled water. A Friedrich condenser and an ice bath served to collect the distillate. It was found that the distillation was complete upon collecting 200 ml. of distillate.

Analysis for volatile carbonyl content. The method of Lappan and Clark *(5)* was modified for the analysis of the volatile carbonyl compounds as follows: One ml. of distillate was placed in a Nash combination blood sugar tube with 2 ml. of 2,4 dinitrophenylhydrazine solution and two drops of concentrated hydrochloric acid. The tube and contents were heated in a boiling water bath for 5 minutes, after which the volume was made up to 5 ml. with carbonyl-free methanol. Five ml. of potassium hydroxide solution was then added and the final volume adjusted to 25.0 ml. with carbonyl-free methanol. The optical density was read at 480 mμ against a distilled water blank treated in the same manner as the sample.

A standard curve was prepared using acetaldehyde as a standard. The results are reported as mg. of acetaldehyde/100 ml. wine. The standard error of estimate of this method was found to be ± 2.16 mg. acetaldehyde/100 ml. of wine.

The carbonyl compounds were isolated as the 2,4 dinitrophenylhydrazones and identified by means of paper chromatography *(4, 6)* and ultra violet adsorption.

Analysis for volatile ester content. Two ml. of 2M hydroxylamine hydrochloride was pipetted into a Nash combination blood sugar tube along with 5.0 ml. of distillate followed immediately with 2.0 ml. of 3.5 N sodium hydroxide solution. After 5 minutes, 2.0 ml. of a 4N hydrochloric acid solution was added. The individual samples were held at this point until all samples and standards of a given assay reached this stage. Two ml. of a 10% ferric chloride in N/10 hydrochloric acid was added, mixed and read at 525 mμ. A distilled water blank was treated in the same manner as the sample and standards.

Ethyl acetate was used as the standard. The results are reported as mg. ethyl acetate/100 ml. wine. A new standard curve was prepared, whenever new reagents were made. The standard error of estimate of this method was found to be ± 0.42 mg. ethyl acetate/100 ml. wine.

Analysis for volatile acidity. Fifty ml. of the steam distillate and a blank using previously boiled distilled water were titrated to a phenolphthalein endpoint with N/10 sodium hydroxide. The volatile acidity was calculated as follows:

$$4\ (\text{ml. alkali for sample} - \text{ml. alkali for blank})\ 6.0 = \text{mg. acetic acid/100 ml. wine.}$$

The volatile acidic components were isolated and identified by silicic acid *(8)* and paper *(7)* chromatography.

Total acidity. Twenty-five ml. distilled water was added to 25 ml. wine. This solution was titrated with N/10 sodium hydroxide to pH 8.30. Results are expressed in terms of per cent tartaric acid.

Storage of the wine. Immediately after the wines were analyzed for their volatile components, the unused portion was transferred to pint bottles. The containers were filled to capacity leaving as little air space as possible in order to simulate the commercial bottling and storage-in-bottles of wine. After 8 months' storage at room temperature (15–35° C.) the analyses were repeated.

[a] Approved for publication by the Director of the New York State Agricultural Experiment Station as Journal Paper No. 1190.

[b] Presented before the Nineteenth Annual Meeting of the Institute of Food Technologists, May 19, 1959.

RESULTS AND DISCUSSION

Changes in the volatile carbonyl content of sherry wine during the baking process. The major carbonyl compound found in sherry wine was identified as acetaldehyde. Trace quantities of acetone and hexaldehyde were also found.

An increase in the volatile carbonyl components occurred during the baking process of both wines (Figure 1). However, a more accelerated increase was

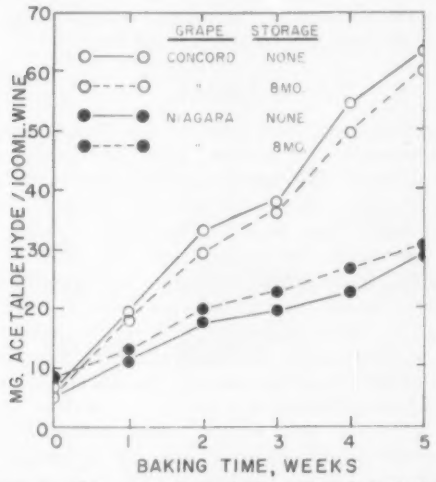

Figure 1. Changes in the volatile carbonyl content during baking and after storage of sherry wine.

observed in wine made from Concord grapes as compared with that from Niagara grapes. The oxidation of ethanol to acetaldehyde may be responsible for a portion of the increase in the volatile carbonyl concentration; however a considerable part of the increase is probably due to a non-enzymatic browning system. The oxygen employed in the baking process may not enter directly into the production of carbonyls by the browning system, although oxygen will act as a catalyst and greatly accelerate the reaction *(3)*. However, this does not exclude oxygen from entering into other associated reactions.

No significant change in the volatile carbonyl concentration was noted after eight months storage (Figure 1).

Changes in the volatile acidic components during the baking of sherry wine. The majority of the volatile acid concentration was found to be composed of formic and acetic acids with a trace of propionic and lactic acids. The volatile acid concentration increased throughout the baking process (Figure 2); however, it should be observed that the volatile acid concentration in Concord sherry wine increased at a much more rapid rate than that in the Niagara wine.

The formic acid could be produced from the degradation of furfural in a non-enzymatic browning reaction *(3)*. The acetic acid could arise from either the browning reaction or oxidation of acetaldehyde to acetic acid. The steady increase in volatile acids accompanied by the formation of formic acid during the baking process indicates that the browning reaction plays an important role in the baking process.

During the baking, differences in behavior of the Concord and Niagara sherries with regard to total acidity and pH was observed. The pH and total acidity of the Niagara wine remained fairly constant while Concord changed radically (Table 1). The increase in total acidity was not explainable by the increase in volatile acidity. An identifying feature of

TABLE 1

The effect of baking time on the total acidity and pH of Concord and Niagara wines

Baking time (weeks)	Concord		Niagara	
	Total acidity (per cent) tartaric acid	pH	Total acidity (per cent) tartaric acid	pH
0	0.45	3.52	0.46	3.21
1	0.48	3.45	0.49	3.21
2	0.50	3.40	0.49	3.21
3	0.52	3.37	0.49	3.21
4	0.54	3.29	0.50	3.18
5	0.57	3.22	0.50	3.18

the non-enzymatic browning system is the rise in acidity and drop in pH. This is caused by the suppression of the "Zwitter-ion" of the amino acid. The carboxyl group of the addition product is then free and titratable.

After storage for 8 months at room temperature, no significant change in the volatile acidic concentration was noted (Figure 2).

Effect of neutralizing the wine before baking. It is a common practice in the industry to neutralize the wine to an acidity of 0.45%, calculated as tartaric acid. The Concord wines, being high in acid, require this neutralization while the lower acid Niagara wines do not.

Three batches of wine consisting of 2 lots of Concord and one lot of Niagara were baked. One lot of

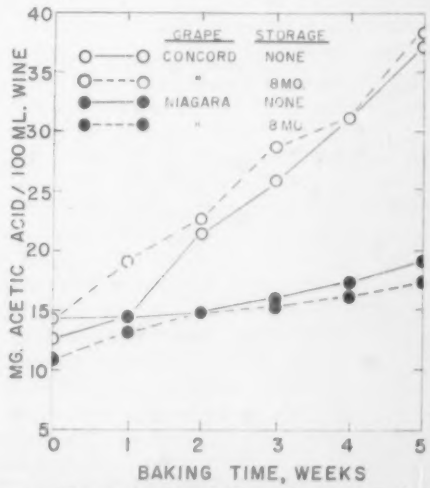

Figure 2. Changes in the volatile acid content during baking and after storage of sherry wine.

the Concord wine was neutralized with calcium carbonate to an acidity of 0.45% ; the remaining batches were baked without any neutralization. The acidity of the unneutralized Concord and Niagara wines was 0.66 and 0.46% respectively. Since alkaline salts accelerate the non-enzymatic browning reaction; neutralization of the wine may accelerate the changes in the volatile constituents.

The changes in the volatile carbonyl content of the non-neutralized wines were closely related (Table 2), while the production of volatile carbonyls in the neutralized wine was accelerated.

TABLE 2

The effect of neutralization of the wine before baking on the production of the volatile and acid compounds

Baking time (weeks)	Volatile carbonyl compounds (mg. acetaldehyde/ 100 ml. wine)			Volatile acids (mg. acetic acid/ 100 ml. wine)		
	Concord neutralized to 0.45% acid	Concord not neutralized	Niagara not neutralized	Concord neutralized to 0.45% acid	Concord not neutralized	Niagara not neutralized
0	7.0	11.3	5.4	13.4	19.9	13.8
1	19.5	14.7	11.6	14.4	24.0	17.4
2	34.5	16.1	14.6	21.6	26.4	17.6
3	37.8	24.0	19.6	25.8	31.2	18.0
4	55.7	30.1	21.0	31.2	33.6	18.5
5	64.3	32.7	27.1	34.2	43.2	19.2
6	71.0	36.1	28.9	40.8	47.4	21.0
Increase	64.0	24.8	23.5	27.4	27.5	7.2

The volatile acids of the Concord wines developed at approximately the same rate, while those of the Niagara wine increased more slowly (Table 2). These data would further confirm the importance of the role that the browning reaction plays in the production of sherry wine.

Changes in the volatile ester content of sherry wine during baking. The volatile ester content of sherry wines was the least changed of any of the volatile constituents studied (Figure 3). The slight increase could be explained by the esterification equilibrium of alcohol and acid. It should be noted that the volatile ester content of the Niagara is higher than the Concord. This is the only volatile component studied, that shows a higher developed concentration than Concord.

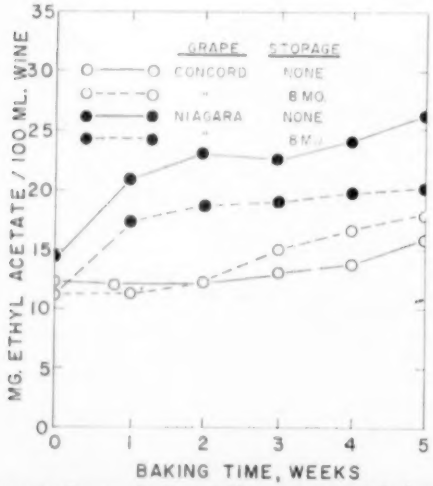

Figure 3. Changes in the volatile ester content during baking and after storage of sherry wine.

Another characteristic of the volatile esters of Niagara sherry is that they are the only group which showed a change in storage. The esters of Concord wine showed no appreciable difference on storage; the Niagara esters decreased significantly. No explanation for the decrease in the volatile esters of Niagara wine can be advanced at the present time.

SUMMARY

Wines prepared from Concord and Niagara grapes were processed into sherry wine by the Tressler baking process. The changes occurring in the volatile carbonyl, ester and acid content were followed through the baking proces. The major volatile carbonyl compound was isolated and identified as acetaldehyde. Slight traces of acetone and hexaldehyde were also present. The major volatile acids were tentatively identified as formic and acetic acids. Propionic and lactic acids were found in trace amounts.

During the baking process, the volatile carbonyl and acid content increased at a rapid rate in the Concord wine. A similar increase was noted in the Niagara wine except the rate of production was approximately one-half that of the Concord. The non-enzymatic browning reaction is advanced as a possible mechanism for the formation of these compounds.

Comparison bakings of Concord wine neutralized to 0.45% acid and of Concord and Niagara wines not neutralized before baking were performed to determine the effect of the presence of alkaline salts in wine during baking on the volatile acid and carbonyl production. The volatile carbonyl content of the Niagara and the non-neutralized Concord wines increased at approximately the same rate, while the rate of increase of the volatile acid content of the Concord wines both neutralized and non-neutralized were similar. These data further confirm the role of the browning reaction in the processing of sherry wine by the baking process.

Of the volatiles measured, the esters increased the least in any group. The ester increase in the Niagara wine was greater than in the Concord. The ester content of the Concord wine appeared to remain unchanged after eight months storage; however, those of the Niagara gave a significant decrease after eight months storage. No explanation of this decrease can be advanced at the present time.

No appreciable change after eight months storage was noted in the volatile carbonyl or acid content in either the Concord or Niagara wines.

Acknowledgment

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Diagnostic Sanitation Analyses in Food and Drug Control*

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(Manuscript received July 18, 1959)

Much has been written about food cleanliness and insects; about the aesthetic and health aspects of food sanitation; about the improvements in food sanitation that have been made during the past several years *(14, 15)*. It is our belief that most people in this country associate insects with filth and insanitation and there is a preference for foods that are as free as practicable from insect debris.

The development of new pesticides and pest control practices have brought about enormous advances in insect control during the past several years and these advances continue unabated. Associated with the use of pesticides to control insects, there is now a widespread recognition of the importance of food plant sanitation in insect control. Sanitation is now an integral part of food industry programs designed to reduce the possibility of food contamination by insects *(2)*.

Major aspects of sanitation developments over the past several years have been the investigations and regulatory activities of the U. S. Food and Drug Administration *(1, 14)*. Since the gradual unfolding of the insect and insect fragment program about 1935, seizures and prosecutions have been, and continue to be, based on the presence of insects and insect filth *(3)*. Such Food and Drug enforcement has not only removed violative merchandise from consumer channels, but has provided an incentive to clean food production. However, regulatory pressure alone would not have brought about the industry-wide improvements that now exist without the laboratory and technological developments of the past several years. Without minimizing modern advances in food technology which have been major factors in clean food production, the discussion before us now is concerned with the development of laboratory-analytical procedures, specifically those microscopic-analytical procedures which are used today in analyzing foods for extraneous materials *(5)*. Laboratory techniques to determine the presence or absence of insect filth have been necessary in the move forward to reduce contamination.

The beginnings of food microanalyses for insect contamination were concerned with the detection of whole insects such as maggots in blueberries and cherries, and insect larvae in flour and meal. These early findings resulted in widespread legal actions and the establishment of industry-wide programs to reduce contamination. In the chronology of this work, field and manufacturing plant observations showed that raw agricultural products containing insect larvae were entering consumer channels. This observation led to the oil flotation principle for the recovery of *insects*, and was followed shortly by the application of this principle to the recovery of insect *fragments*. In the years that followed, the detection of insect

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fragments in foods has become a valuable tool in the hands of food processers and regulatory agencies charged with maintaining the cleanliness of the food supply *(7)*.

Howard and others recognized that, in addition to being able to distinguish between insect debris in foods and the food particles themselves, they recognized that certain insect pieces originated from specific insects *(13)*. However, this possibility, and more especially, its significance in food control operations, lay unexplored until 1949–50 *(6, 12)*. Since that time, marked advances have been made in the identification of insect fragments. These advances are continuing *(4, 11)*.

Recent developments on the identification of insect *fragments* as distinct from the mere recognition that debris is not a normal fruit or vegetable constituent, emphasizes that the current work on diagnostic sanitation analyses is proceeding rapidly in two parallel directions:

1. The identification of *insect pieces* as originating from specific *insects*, gives information far beyond that which could be obtained if the insect were not so identified *(8)*. For example, a laboratory finding of Drosophila eggs, maggots, or maggot parts in a mixed vegetable baby food would call for a different control program than would a laboratory finding of aphid fragments.
2. The *recognition* of insect fragments, as such, by specific insect fragment morphology, bases insect fragment recognition on basic biological criteria. In other words, if we make use of the micro-morphological characteristics of *insects* in recognizing *insect fragments*, then we are basing the analysis on the material which is fundamental to the entire problem *(9, 10)*.

"Diagnostic sanitation analysis" as applied to insect fragments, makes use of the specific anatomical, morphological, and micro-morphological details that characterize the insect species. All too often in the past, training in insect fragment recognition has begun with sample analysis and insect *pieces*. The systematic approach which we are proposing here begins with the insects from which the fragments are derived. Let us show you what we mean.

Take the material in Figure 1 as our first example. We keep recovering articles like this in routine analyses. It does not seem to be ordinary plant tissue debris and it does have a similarity to pictures that we have seen of an insect larva thoracic leg. It is tapering and has joints and that "may be about enough" to characterize it as "insect."

Insect antennae are elongated segmented structures (at least in some cases). We may have some doubts about the appearance of the material in Figure 2, but since we do keep finding it in insect-infested grain and seeing it over and over again, we finally become convinced that it is not plant debris but is, in fact, a piece of insect. Although we start counting it with some uncertainty, as the months go by we realize more and more that it "couldn't be plant" and our

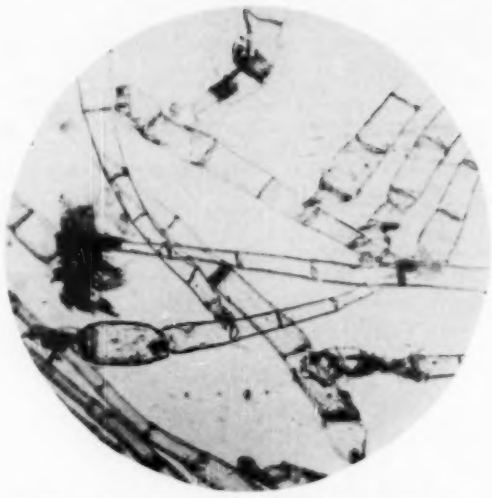

Figure 1. Tapering segmented debris from filter paper.

Figure 2. Segmented jointed structure from grain product.

confidence increases that it must be insect. After all, it does have many of the characteristics used in some laboratories to characterize insect debris. But, is it really? Some of you will begin to recognize that this type of analysis is akin to a chemical identification based on an all-negative approach without a specifically characteristic test.

Let us attack this insect fragment recognition problem the other way around. Let us start with the insect. What insect? We are not dealing with "any old insect." Contamination in a particular food field usually involves a limited group of insects so that in each food field we are concerned only with specific pests. Insects are selective in their habits and this permits us to be selective in the insects to be studied. In stored cereal grain, one of the insects that we would study would be the granary weevil: egg, larvae, pupae, and adult. We will dissect it step by step,

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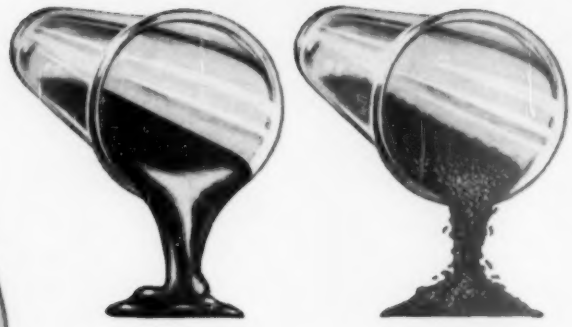

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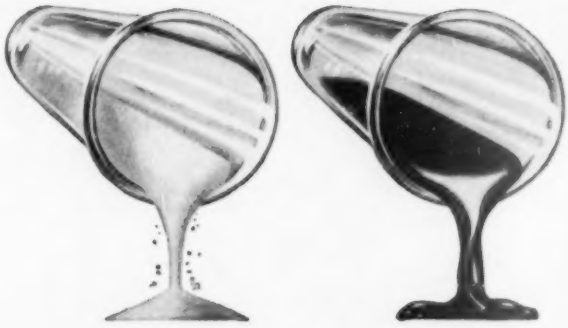

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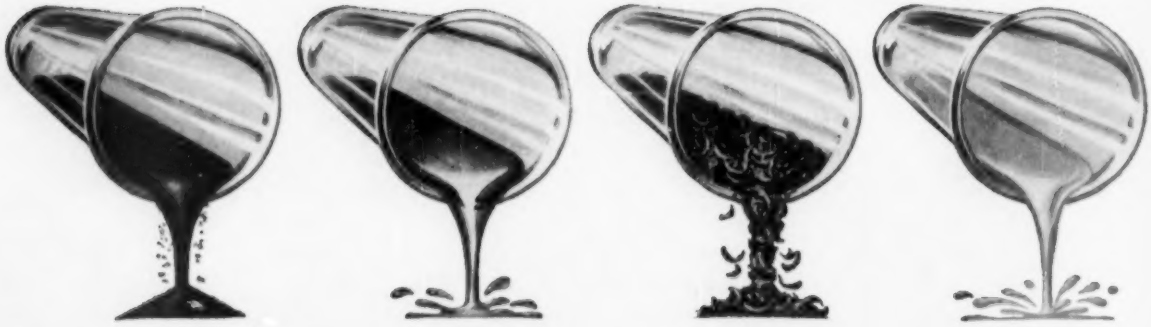

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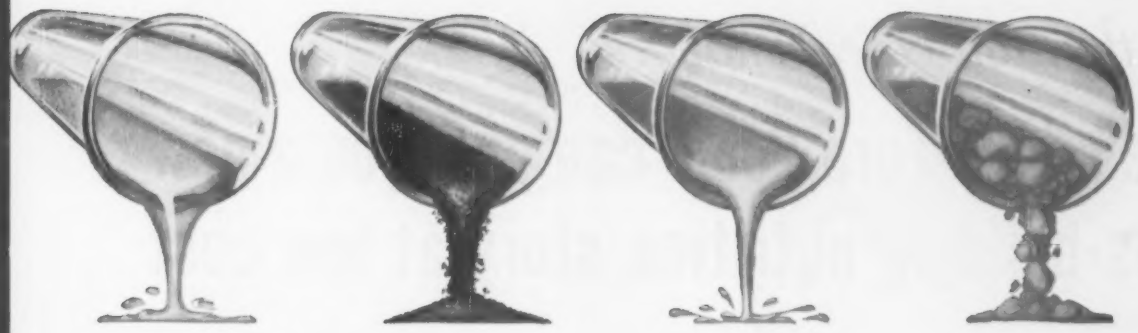

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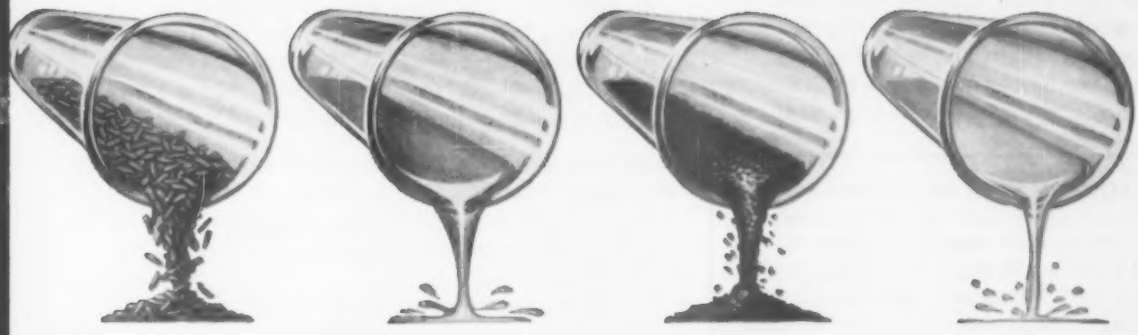

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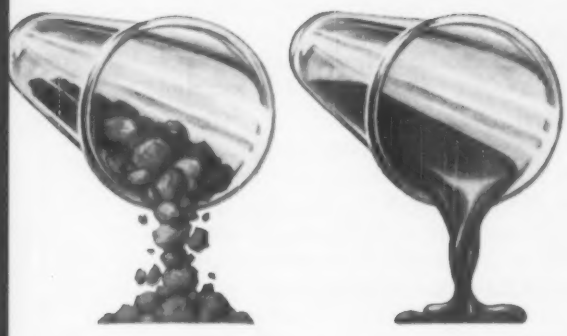

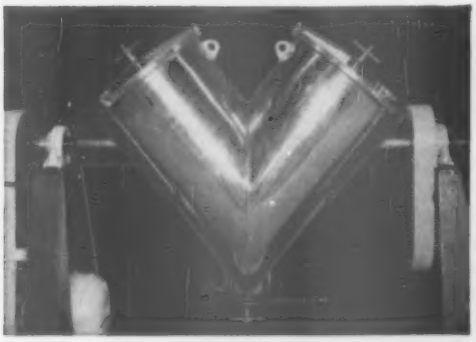

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FREE PRE-TEST OFFER. You can preview blending economies at our Laboratory. Pre-testing predicts savings in processing and handling and realistically demonstrates the unique performance of this blender.

Our pre-test facilities for blenders – and also for P-K Vacuum Tumble Dryers – are at your disposal. Send or bring your test materials. For complete information call (Stroudsburg – Hamilton 1-7500) or write George Sweitzer at our East Stroudsburg Headquarters, 1609 Hanson Street.

Patterson Kelley

Chemical and Process Equipment Division, East Stroudsburg, Pennsylvania

Attention cereal makers:

Here's how Tora Food® can give you a new sales-building nutrition story at low cost

If you need a powerful new story to spark the sales of your cereal, Tora Food (Red Star's brand name for Torula Yeast U.S.P.) is your answer. And you can actually *save* money. Here's what we mean:

How will Tora Food improve nutritional content of cereal? Here are some specific nutritional factors housewives know and look for in cereal. This chart shows you how Red Star Tora Food increases these factors in a typical cereal—corn meal.

PER 100 GRAMS OF CORN MEAL

	Corn meal as is	Corn meal plus 3% Tora Food
Protein	9.00 grams	10.50 grams
Vitamin B_1	0.30 milligram	0.66 milligram
Vitamin B_2	0.08 milligram	0.20 milligram
Niacin	1.90 milligrams	2.80 milligrams

What totally will Tora Food add to cereal?
(At a level of 3# to 100#)

Vitamin B_1	163.5 milligrams worth
Vitamin B_2	54.5 milligrams worth
Niacin	408.6 milligrams worth
Vitamin B_6	40.8 milligrams worth
Para-amino benzoic Acid	20.4 milligrams worth
Pantothenic Acid	150.0 milligrams worth
Folic Acid	95.3 milligrams worth
Choline	4.8 grams worth
Inositol	5.4 grams worth
High quality Protein	1.5 lbs.

Here is a nutritional "barrage" that can't help but impress the nutrition-conscious housewife.

How can Tora Food actually save you money? The ingredients listed above would cost you 87.33¢ at current price levels, if you bought them individually. You get these *same* ingredients in the *same* amounts for only 54¢ in Red Star Tora Food. That's 33.33¢ saved. (Incidentally, the same amount of brewer's yeast would cost you between 72¢ and 84¢.)

In addition, Tora Food saves you money on handling and inventories. Instead of buying, storing, handling and keeping books on 10 or more different ingredients, you need handle only *one* when you use Red Star Tora Food.

How else will Tora Food improve saleability of cereal? Tora Food will intensify the flavor of your cereal. It has a mild, pleasant flavor with the ability to enhance the natural flavor of the product to which it is added.

Furthermore, Tora Food is an antioxidant and helps give your cereal longer shelf life.

Who besides cereal makers can use Tora Food? Almost any food processor. Here we've talked specifically about cereal makers, but baby food processors are already using Red Star Tora Food successfully. And here are some other types of processors who can use Tora Food to big advantage: spice, soup, chocolate, peanut butter, sauce and gravy, health food, smoked yeast and pharmaceuticals.

If you are a cereal maker (or *any* food processor) who wants a new sales-boosting nutrition story, write to us. We'll be happy to show and discuss with you work and analysis that has been done. Or if you prefer, we'll be happy to have a nutritionist call on you. Write to the address below.

Nutritional Division

RED STAR YEAST & PRODUCTS CO.

Milwaukee 1, Wisconsin

beginning at the head and going back through the insect region by region (head, thorax, abdomen); area by area (prothorax, mesothorax, metathorax); sub-area by sub-area (notum, pleuron, sternum); part by part (legs, wings) until finally, with detailed knowledge of all the structures, we arrive at the piece to be used as our example.

An entire leg, Figure 3, represents an obvious insect fragment. To anyone with even an elementary knowledge of biology—in fact, almost from the scientific knowledge available in the daily press—it should be relatively simple to recognize the leg. About all that is needed to make the analysis is the correct microscope and an adequate illuminator.

As the analyst has, now, already done systematically with other structures studied, he will now isolate

Figure 3. Beetle leg.

the individual sclerites, in this case, the leg segments. Let us look at a first segment, the coxa, Figure 4, in its complete form.

If the coxa were on a filter paper its identification would be more difficult than that of the whole leg, especially if you have never seen a coxa before. But, even without this background you may recognize this as something special that "looks like" insect and perhaps count it. However, accurate characterization would be based on a knowledge of the manifold characteristics that are present on various insect fragments. However, the purpose of this paper does not necessitate going through all the details of shape, and surface sculpturing, but to examine species characteristics that are used in insect fragment recognition and identification. A good example is the weevil coxal groove (Fig. 4, see arrow) that articulates in the thoracic coxal cavity. Coxal fragments with this groove

Figure 4. Weevil coxa.

are real "repeat performers" in the examination of foods that contain granary weevil contamination.

Figures 5 and 6 will tell and illustrate the remainder of the story. Note that the finer and finer breakdown of the coxa and the study of the groove area of the coxa permits the analyst to identify with absolute certainty fragments coming from this area of the leg segment (coxal groove).

This is the story. In a way, it is simplicity in itself. Although only a small area of the insect fragment problem has been discussed, this has been done purposely to focus on *one* salient point of insect fragment recognition and identification. We identify insect fragments, not by attempting to recognize the infinite variety of sizes, shapes and forms in which they appear but through a study of the insects from which they were derived. A knowledge of the insect is a simple, organized, and sure key to the recognition of insect fragments. The recognition of insect fragments

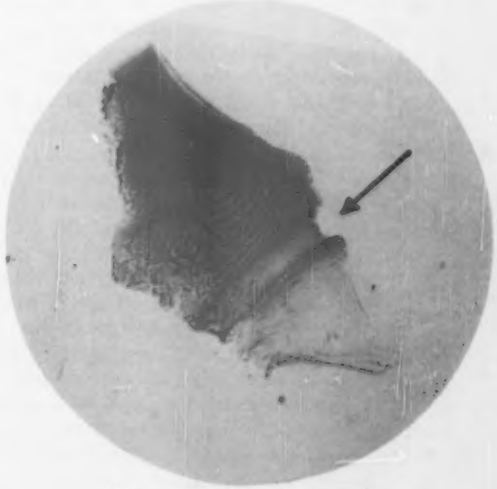

Figure 5. Weevil coxa fragment.

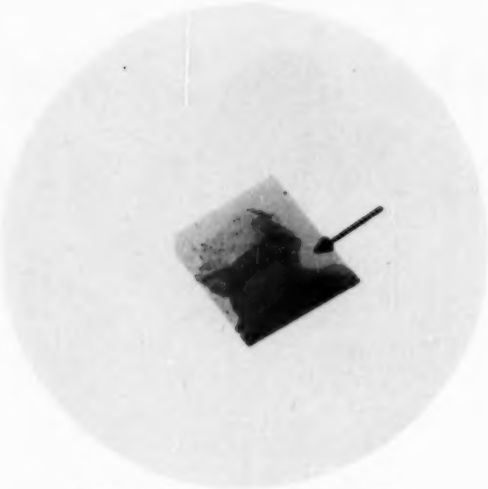

Figure 6. Smaller weevil coxa fragment.

was partially explained when we recognized the leg as an insect appendage; the coxa, as a basic leg component; and when we recognized the characteristics of this structure. Fragmentation beyond this basic unit naturally results in variously shaped pieces of cuticle which bear little over-all resemblance to the intact structure, but which still retain the *micro*-morphological characteristics which we now know to exist on the structure itself. In many respects, this approach to insect fragment analysis has been oversimplified. There are many morphological details which are considerably more complex, but the concept embracing this approach to insect fragment work is relatively simple. It is based on a tangible systematically organized foundation, the insect, with each fragment situation depending only on the insect or insects which concern the particular food field. When we know the insect we can diagnose the etiology of the contamination and so interpret its significance.

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The Stabilizing of Tin-Plate Surfaces[a]

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THE OXIDE FILM normally present on tin, although protective to some degree, readily grows to such an extent that discoloration of the surface is easily discernible. This oxidation and the accompanying discoloration, commonly called "yellow-stain," can occur during storage in warehouses under humid conditions or during the baking operation that follows lacquering or enameling. However, it is not only the change in the appearance of the tin plate that is objectionable; the oxide film formed during warehouse storage can prevent the proper adherence of some lacquers and lithographing inks to the tin surface, and can cause difficulty during modern, high-speed soldering operations in the manufacture of cans.

These and related problems, such as the prevention of the sulfide stain that occurs when some foods are packed in tin cans, have been studied by numerous investigators, some of whom have patented their findings. Also, other patents have been issued for processes that were specifically designed for other metals but that were claimed to provide protection to tin. The most important of these patents and publications are summarized in the remarks that follow.

In 1931, S. R. Mason *(13)* patented a process in which metallic surfaces were cathodically treated in a solution containing sodium dichromate or chromic acid. This process was comparatively unknown to the tin-plate industry until recent years. In 1935, H. S. Schutte *(20)* patented a process in which tin plate was treated in a hot dilute solution of potassium permanganate to decrease sulfide staining. In 1940, C. G. Sumner *(21)* patented a process in which an anodic—cathodic-anodic treatment was used to minimize the sulfide staining of tin plate. Also, in 1940, R. Kerr *(12)* published the results of an investigation in which tin plate was treated in an alkaline solution containing chromate or certain other chemicals. In 1943, W. O. Cook and H. E. Romine *(6)* obtained a patent for a process in which tin plate was cathodically deoxidized in a sodium carbonate solution to improve the resistance to baking discoloration. In a second process patented by Cook and Romine *(7)* in 1943, tin plate was anodically oxidized in a sodium carbonate solution to minimize sulfide staining. In the same year, F. E. Rath *(19)* patented two processes, one using a solution of sodium phosphate, phosphoric acid, and chromic acid, and the other using a solution of caustic soda and chromic acid. In general, the above processes either were intended as answers to specific problems, though lacking in other respects, or were comparatively slow processes intended for the treating of cans or flat sheets. None of the processes were entirely suitable for commercial use by the tin-plate manufacturer.

The advent of World War II gave impetus to the search for a satisfactory treatment. To conserve tin, it was necessary to substitute lacquered electrolytic tin plate for much of the hot-dipped tin plate customarily used. However, because the oxide stability and the lacquering properties of untreated electrolytic tin plate were poor, it was necessary to treat the tin plate to improve these properties.

The most convenient and practical treatment of several that were investigated at that time was a simple chromic acid treatment developed by J. G. Donelson and E. E. Ketchem *(8)*. This treatment, which was originally intended for application to scratch-brushed tin plate, also improved the lacquering properties and the resistance to discoloration of unmelted (matte) tin plate and of melted (flow-brightened) tin plate. The chromic acid treatment has been widely used and has been instrumental in making feasible the substitution of electrolytic for hot-dipped tin plate. In 1942, line speeds were about 300 feet per minute; however, by 1946, line speeds were 600 to 1000 feet per minute, and electrolytic lines were already being designed to operate at even greater speeds. For such high-speed lines it was anticipated that a more rapid and more effective treatment would be required.

That others were also interested in developing a more rapid and a more effective treatment for tin plate is evident from the patents and publications of the past ten years. For instance, in 1948, C. E. Glock *(10)* reported that subjecting the surface of flow-brightened tin plate to a light rubbing action improved the results obtained by a subsequent cathodic treatment in an alkaline phosphate chromate or a chromic acid solution. In 1950, A. F. Prust *(18)* reported that a steam atmosphere protected a cathodically treated surface between treating, rinsing, and drying. In 1952, W. D. Poole *(16, 17)* reported that cathodic reduction in an alkaline solution, rinsing with water, rinsing with hot dilute chromic acid, and again rinsing with water produced a satisfactory surface on tin plate. Also in 1952, a patent was granted for one of the processes described in this paper *(15)*. More recently, in 1954, Britton and Angles *(4)* improved the treatment originated by Kerr *(12)* now known as the Protectatin Process and used for treating cans in Europe.

The foregoing review of previous work covers only the key patents and publications that constitute the historical background of research on tin-plate surfaces and is not intended as a complete bibliography. It also acknowledges contemporary research that has led to processes now being used commercially *(8, 15, 17, 18)*.

[a] Presented at the Nineteenth Annual Meeting of the Institute of Food Technologists, Philadelphia, Pennsylvania, May 20, 1959.

The present paper reports investigations to minimize baking discoloration and to stabilize tin-plate surfaces for warehouse storage.

TEST METHODS AND SAMPLE PREPARATION

Preparation of tin plate for laboratory experiments. For bench-scale work, commercial electrolytic tin plate, which had been treated with chromic acid and oiled, was used except, as is specifically mentioned, for instances where untreated tin plate was employed. To obtain results similar to those obtained with freshly produced untreated tin plate, it was necessary to degrease the tin plate with solvent and then cathodically deoxidize and clean the surface in a dilute solution of sodium hydroxide or sodium carbonate (2 to 2.5 g. per liter). The cathodic cleaning was accompanied by evolution of hydrogen and was continued until the tin surface could be uniformly wet with water. If the tin surface became etched during the cathodic cleaning, the specimen was discarded.

The bake test. Numerous tests are available for use in evaluating tin-plate surfaces, but the main criterion used in the present work for the preliminary screening of the various treatments was a bake test in which the tin plate was held in air at 420° F. for 1 hour. At room temperature, the rates of outward diffusion of tin ions and of the inward diffusion of oxygen through the normal oxide film are not very great. However, at 420° F., the diffusion rates are comparatively rapid, and heavy yellow-stain will form on untreated tin plate within as short a time as 20 minutes. On the other hand, treated tin plate is often unchanged in appearance even after 1 hour of exposure to the same conditions.

The comparable amounts of oxide on the tin surface were measured before and after baking by using the electrolytic reduction method described later in this section. Further, since the degree of visible discoloration was also of primary interest, this was arbitrarily rated on a scale ranging from 0 (indicating no discoloration) to 10 (indicating heavy discoloration, such as would be formed on deoxidized, untreated tin plate exposed to the same conditions at the same time).

The humid-storage pack test. Tin-plate specimens approximately 9 by 6 inches were assembled into a pack about 1½ inches thick and stored at 85% relative humidity and 100° F. Every 2 weeks, three adjacent specimens were removed from the interior of the pack. These were graded for visible discoloration, and the oxide values were determined by an electrolytic reduction method.

Oxide determination. A coulometric method was used to measure the comparable amount of oxide on the tin plate by electrolytic reduction in 0.1 M potassium chloride at a constant current of 1.83 milliamperes per square inch. A platinum grid was used as the anode. The potential remains constant until the reduction is completed, and then changes to the potential of hydrogen. The time required for the change in the potential to occur is a measure of the amount of oxide present. The data are presented as millicoulombs per square inch of surface required for reduction.

This method was first used on tin plate in 1940 by J. G. Donelson and was patterned after the electrochemical reduction procedures used in investigating oxide films on other metals by Miley *(14)*, Vernon *(23)*, and Campbell and Thomas *(5)*. Quite recently, after the completion of the development work described in this paper, the procedure was studied by Frankenthal, Butler, and Davis *(9)*, and by Willey and Kelsey *(24)*, and changes were recommended for greater accuracy.

The sulfide test. To indicate the resistance of the tin plate to sulfide staining, a simple test was devised in which the tin-plate specimens were immersed in a 2% solution of sodium sulfide for 3 hours at room temperature. The degree of staining that occurred was arbitrarily rated by use of the following scale: 0 *(no stain)*, 3 *(light stain)*, 6 *(medium stain)*, and 10 *(heavy stain)*. *Heavy stain* would be on the order of that formed on deoxidized, untreated tin plate. This test was sufficient for screening purposes.

The solder capillary-rise test. Specimens 1 by 3 inches were folded lengthwise to form a tube (3 inches long) having a narrow, elongated teardrop cross section. The tin-plate surfaces at the apex of teardrop were in contact, forming a narrow capillary. The tubes were fluxed by dipping them into melted palm oil, and were then inserted into a bath of molten solder (70–30 solder at 530° F.) to a predetermined depth, held for 1 minute, and quenched. The height to which the solder rose above the bath level in the capillary was measured. This test, devised by Allen *(1)*, is believed to indicate the ability of solder to penetrate into the side seam of a tin can better than any other laboratory test now known.

The vinyl-chloride lacquer test. This test was used to show whether commercially treated tin plate had a continuous protective film at the time of production (or shortly thereafter). The test is based upon the thermal decomposition of a clear, nonstabilized vinyl-chloride lacquer when it comes in contact with a tin surface. Thus, when a continuous protective film exists between the tin surface and the lacquer, decomposition of the lacquer does not occur and a clear coating is produced. But, when freshly abraded areas are exposed to the lacquer, the lacquer becomes black in appearance at the point of contact. (This test is not valid for tin plate that has been in storage, since oxide films that form on abraded areas during even a few weeks of storage are sufficient to prevent the local decomposition of the lacquer.)

The vinyl-chloride lacquer was applied to the tin-plate specimens by means of a Fisher-Payne Dip-Coater. The desired coating weight was 8 mg. per square inch. The lacquered panels were held in air at room temperature for at least 10 minutes and then oven-cured at 330° F. for 10 minutes.

Because the acid fumes from the decomposition reaction can also cause further decomposition of the lacquer, the curing was done in an air-circulating oven to ensure continuous removal of the fumes from the oven atmosphere. For the same reason, only a few specimens were cured at one time (about 4 panels, each 3 by 6 inches, can be cured at one time in a 1-cubic-foot oven).

PROCEDURE AND DISCUSSION

Bench experiments. From previous experience it was known that although the oxide film on a tin surface can minimize sulfide staining, the oxide film continues to grow during storage or during baking. To obtain an effective treatment, it was necessary, therefore, that the existing oxide either be stabilized or entirely replaced with a more stable film.

As a first step, identification of the oxide films normally present on electrolytic tin plate was attempted. Electron-diffraction methods failed to do this, but did suggest that these thin, invisible oxide films are amorphous rather than crystalline. This observation is in agreement with the findings of other investigators *(2, 3, 11)*, who reported that in the thermal oxidation of tin there is a critical temperature between about 266° F. and 338° F., below which only amorphous oxide is formed. Since these results indicate that an amorphous oxide always forms first *(11)*, the difficulty in identifying the thin oxide film normally present on tin plate is explained. It is believed, however, that the oxide immediately adjacent to the metal is stannous oxide and that some stannic oxide may be present in the exterior surface.

Although the composition of the oxide on the surface of tin plate was not established, it was known that the tin oxides are amphoteric and can form heteropoly acids and complex combinations with the radicals of vanadic, tungstic, and molybdic acids *(22)*. These are members of a group of acidic oxides that exhibit a strong tendency to polymerize, to form autocomplexes of high molecular weight, and to exist in two or more stages of valence within the same solution. Chromic and permanganic acids are also members of

this group, although permanganic acid exhibits little, if any, tendency to form complexes. On the other hand, phosphoric, boric, and arsenic acids are known to serve as other acid radicals in forming heteropoly acids with the above acid-metallic oxides. Since most of these compounds are capable of polymerizing and of interacting with the tin oxides, it was believed that one or more would aid in forming a thin, continuous film that might serve as a barrier to retard further oxidation of the tin.

Accordingly, solutions containing these compounds, either alone or in simple combinations, were used experimentally for immersion treating and for electrolytic treating of tin plate. All possible combinations were not studied. In these experiments, chromate, vanadate, molybdate, tungstate, and mixtures of these with phosphate were promising. However, because of better availability and lower costs, development work was limited to chromate and chromate-phosphate solutions.

In one series of experiments, untreated tin plate was immersed in 0.1 M sodium dichromate solution for 5 seconds at room temperature, rinsed with water, and dried. This simple treatment improved the resistance of the tin plate to the discoloration that forms when the tin plate is baked for 1 hour at 420° F. However, the discoloration that did occur was distributed over the surface in a nonuniform pattern of spots, an indication that the continuity and structure of the protective film might be adversely affected by the oxide beneath it.

Consequently, different methods of removing the existing oxide before passivating the tin plate were experimented with. Of several methods tried, electrolytic reduction was the most promising. The reduction was accomplished in a solution containing 2.5 g. per liter of sodium carbonate, residual alkali being removed by water rinsing. The tin plate was then passivated in 0.1 M sodium dichromate as described in the preceding paragraph. Tin plate treated in this way was more uniformly resistant to baking discoloration than the specimens that had not been deoxidized before treating. Subsequently, it was learned that the degree of protection obtained could be improved by increasing the treating time or the temperature of the treating solution, but that increasing the concentration of the treating solution had little effect. However, the degree of protection obtained with rapid treatments of the order of 1 or 2 seconds was not thought to be sufficient for commercial purposes.

Although the treatment described above was not considered satisfactory for commercial use, the degree of protection was superior to that obtained previously. As a further step, therefore, the electrolytic reduction was next performed directly in the dichromate solution. Upon cessation of the cathodic action, reoxidation would then take place while the tin surface was in contact with the passivating solution. Protective films formed in this way had good resistance to baking discoloration even though the treating time was very short.

Because slightly thicker or denser films might be more resistant to discoloration and perhaps less sensitive to handling, the possibility of forming such films by carefully controlled anodic oxidation, subsequent to the cathodic reduction and in the same passivating solution, was investigated. The results of many experiments have shown that to produce the most satisfactory films, the anodic current density should be low. For example, when anodic oxidation was continued for ½ second, films formed by using 5 to 6 amperes (2.5 to 3 coulombs) per square foot had good resistance to storage stain and to baking discoloration, and were reasonably resistant to sulfide stain and to abrasion. Anodic films formed by using 5 to 6 amperes per square foot for 1 second (5 to 6 coulombs) had somewhat better resistance to abrasion, to sulfide staining, and to attack by dilute acids; however, the adherence of a few lacquers is apparently affected by any degree of anodic treatment. On the other hand, films formed by using anodic current densities of about 30 amperes per square foot for ½ second (15 coulombs) were somewhat less satisfactory, and films formed by using current densities such as 90 amperes per square foot for ½ second (45 coulombs) were more porous and less protective.

Attempts have been made to identify the individual components of the protective films by electron-diffraction methods. Although these were not successful, it was observed that the films are probably amorphous. Other investigators *(3)* have recently succeeded in stripping the films but have not identified the compounds present. The authors suggest that the films are largely solid, insoluble complexes of indefinite composition, and it is doubtful, therefore, whether the films can be defined with a satisfactory degree of certainty. The effect of the cathodic reduction of the tin oxide and also of the nascent hydrogen produced probably leads to the formation of hydrated chromic oxide in the solution film at the tin surface. Also, upon cessation of the cathodic reduction, particularly when followed by anodic oxidation, stannous ions would be formed. However, the stannous ions would, in turn, be largely oxidized to stannic ions with an accompanying reduction of additional hexavalent chromium. The protective films, therefore, probably contain tin in more than one stage of valence, whereas the chromium is thought to be largely in the trivalent form.

PILOT-LINE TRIALS

After completing the bench-scale experiments discussed above, a number of pilot-line trials were made. These were primarily intended to establish the desirability of installing the treating process on a commercial line and to compare the protection offered by different treatments. This pilot line operated at a speed of 450 feet per minute in tinning and treating steel strip 6.5 inches wide. The schematic arrangement of the units in the line is shown in Figure 1. Two treating tanks were available for the trials. The first immediately preceded and the second immediately followed the melting tower (where the tin coating is heated slightly above the melting point and

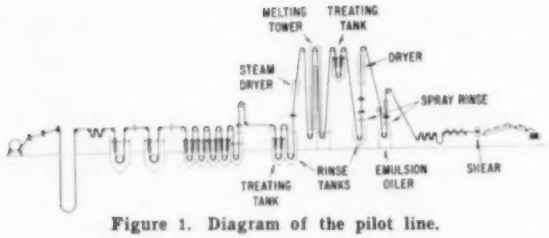

Figure 1. Diagram of the pilot line.

then quickly cooled by immersion in water). Both treating tanks were equipped for either chemical or electrochemical treating, and the arrangement of the tanks permitted experimental filming either before or after melting, or at both times.

Data for a few of the treatments that were produced on the pilot line are shown in Tables 1 and 2. A comparison of the data for tin plate treated by other processes, Table 1, with the data for tin plate given the cathodic or the cathodic-anodic treatments directly in a dichromate solution, Table 2, illustrates the superiority of the latter two treatments in minimizing the discoloration caused by baking or by contact with solutions containing sulfur. The data also show that these two treatments did not adversely affect the solderability of the tin plate.

TABLE 1

Comparison of chemical and electrochemical treatments (pilot line)

Trial	Treatment	Oxide values, millicoulombs/sq. in.		Visible discoloration after baking*	Sulfide discoloration*	Solder capillary rise, in.
		As made	After baking			
1	Untreated	20	100	10	10	1.15
2	Chromic acid treated	16	65	10	10	0.55
3	Cathodic treated before melting	13	65	2	6	0.73
4	Cathodic treated before melting, chromic acid after	15	50	2	6	0.65
5	Cathodic cleaned and chromic acid treated	15	29	3	10	0.70

* 0 = no discoloration, 10 = heavily discolored.

Treating conditions:

Trial 2. Chromic acid 0.7% at 180° F.

Trial 3. 30 amp./sq. ft., in 0.5% Na_3PO_4 and 0.2% $Na_2Cr_2O_7 \cdot 2\ H_2O$ at 100° F.

Trial 5. 30 amp./sq. ft., in 0.5% Na_3PO_4, H_2O rinse, chromic acid treat, H_2O rinse.

TABLE 2

Electrochemical treatment in 1.5 per cent dichromate (pilot line)

Trial	Treatment	Oxide values, millicoulombs/sq. in.		Visible discoloration after baking*	Sulfide discoloration*	Solder capillary rise, in.
		As made	After baking			
1	Chromic acid control	15	80	10	10	0.45
2	Cathodic only	7	18	0	0	0.88
3	Cathodic-anodic, 3 coulombs	9	18	0	0	0.92
4	Cathodic-anodic, 5 coulombs	11	22	0	0	1.00
5	Cathodic-anodic, 10 coulombs	15	27	0	0	0.95

* 0 = no discoloration, 10 = heavily discolored.

Treating conditions:

Cathodic current density: 90 amp./sq. ft.

Line speed: 450 f.p.m.

Solution temperature: 100 F.

For the control lot, the solution contained 0.7% chromic acid at 180° F.

COMMERCIAL ADAPTATION

During the commercial adaptation of these processes, it was learned that abrasion arising from mechanical sources could be a detrimental factor. In fact, observations indicated that the protective films formed by all treatments are apparently fragile when freshly prepared, although partial removal of a protective film is not as apparent with an inefficient treatment as with a good treatment. Fortunately, it was not difficult to minimize mechanical abrasion to the point where it was no longer of commercial significance. An example of an unusually severe abrasion pattern obtained before the elimination of this difficulty is shown in Figure 2. (The long black streak

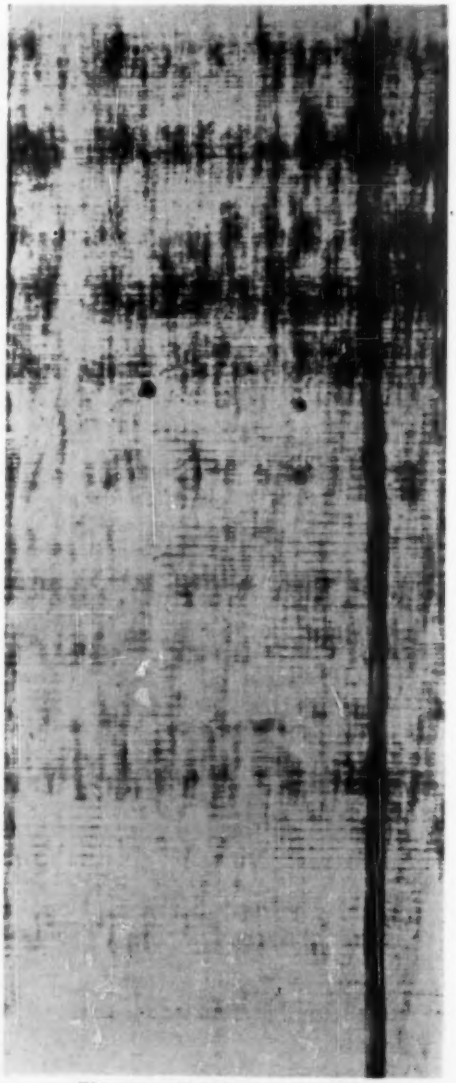

Figure 2. Abrasion of tin plate.

observable in the photograph was made by rubbing the tin surface with a rubber eraser immediately before lacquering in order to show the effect of local removal of the protective film.) On the other hand, the stability of representative samples of dichromate-treated commercial tin plate is shown by the oxide-growth curves presented in Figure 3.

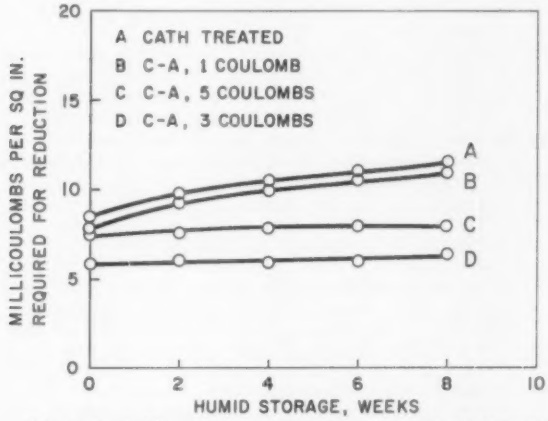

Figure 3. Oxide growth on commercial tin plate, dichromate treating solution.

Results of tests such as those just discussed strongly indicated that the surface stability of commercial electrochemically treated tin plate was very good. The data were obtained, however, by the use of accelerated tests, such as the humid-storage pack test. To determine the effectiveness of the various treatments in preventing surface deterioration under actual commercial conditions, an extensive series of warehouse-storage tests was made. In these tests, bundles of treated tin plate were stored under hot, humid conditions in a warehouse near the Gulf of Mexico.

More than 100 sample lots, including various coating weights of tin and both matte and flow-brightened tin plate, were obtained from 15 tin-plating lines. The variations in surface stability obtained within the various lots of each treatment are shown in Figures 4, 5, and 6, and the humid-storage test results are summarized for each treatment in Figure 7. These data show that commercial tin plate treated electrochemically in dichromate solution has more resistance to warehouse discoloration than tin plate treated in other ways and is remarkably uniform in quality. Also, it was observed that the electrochemical dichromate treatments were effective with both matte and flow-brightened tin plate and that they were the only treatments that adequately protected the heavier tin coatings such as 1.00 pound per base box.

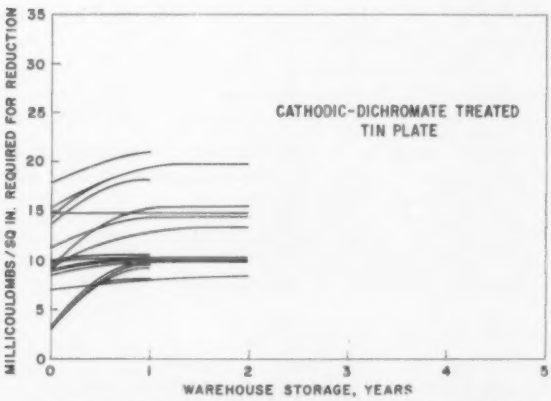

Figure4. Oxide growth during warehouse storage, cathodic-dichromate treated tin plate.

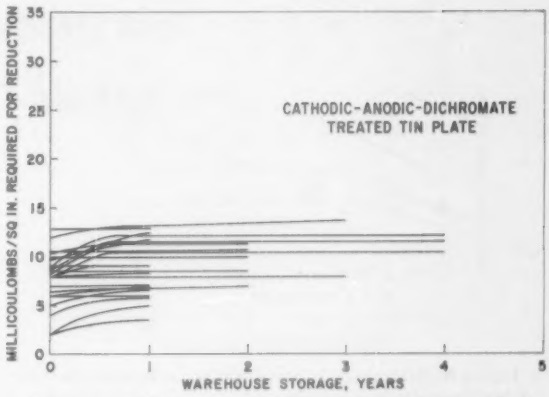

Figure 5. Oxide growth during warehouse storage, cathodic-anodic dichromate treated tin plate.

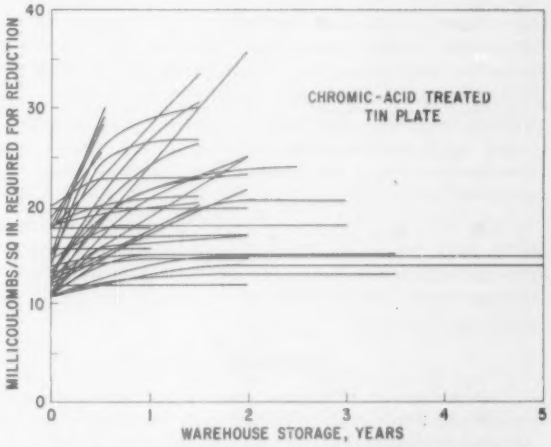

Figure 6. Oxide growth during warehouse storage, chromic-acid treated tin plate.

There are many limiting conditions that must be met in treating tin plate. The protective film must be invisible, must be easily applied and controlled, and yet must offer adequate protection. Also, the film must not adversely affect the life of the can, must not adversely affect the adhesion of the organic finishes used by the can industry, and must not adversely affect solderability.

These restrictions are so broad that some compromise has always been required, regardless of the method of treatment. In the present instance, there are a few lacquer systems that are not entirely satisfactory when used with these electrochemically treated

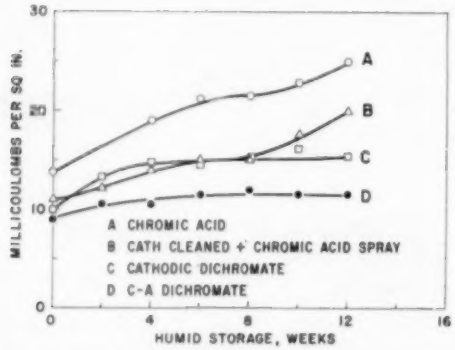

Figure 7. Oxide growth, humid-storage test. Average values for warehouse-storage samples.

films, although the protective film formed by the cathodic treatment is apparently more satisfactory in this respect than that formed by the cathodic-anodic treatment. Also cathodically treated tin plate approaches cathodic-anodic treated tin plate in stability and is considerably more stable than chromic acid treated tin plate. The cathodic treatment is, therefore, being used commercially. However, it is hoped that new lacquers may be developed to replace those few with which the cathodic-anodic films are not entirely satisfactory, so that the superior properties of these films may be fully utilized. Meanwile, research is continuing in an attempt to produce protective films that are satisfactory with all the usual tin-plate lacquers and enamels.

SUMMARY

Treatments to minimize baking discoloration and warehouse deterioration of tin-plate surfaces were investigated. Several reagents were found to be effective for this purpose. Of these, sodium dichromate was the most practical for commercial use. However, the protection obtained is limited if the normal air-formed oxide lies beneath the protective film. Therefore, it is desirable to remove the existing oxide and then replace it with the protective film. This is best accomplished by cathodic reduction in the passivating solution followed by chemical or electrochemical oxidation in the presence of the passivating agent.

Protective films formed on tin plate by either of these methods, though invisible and very small in thickness, provide an effective barrier between metal and oxygen. Films formed by the electrochemical reduction and reoxidation method, however, are more stable, more resistant to sulfide staining, and more resistant to attack by dilute reagents. On the other hand, films formed by this method are not entirely satisfactory with a few lacquers used by the can industry. Although research is continuing in an attempt to produce protective films that are satisfactory with all tin-plate lacquers, it is hoped that new lacquers may be developed that will permit utilization of the protective films most resistant to oxidation.

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Relationships Between pH, Tenderness, and Moisture Levels During Early Post-Mortem Aging of Turkey Meat[a, b]

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FROM PREVIOUS WORK in this laboratory *(8)* it must be assumed that temperature and water play an important role in post-mortem tenderization of poultry meat. Poultry has been shown to tenderize more rapidly in cooler temperatures *(8, 16)*, whereas the reaction has been shown to be opposite in beef *(6, 22)*. Poultry has also been shown to tenderize more rapidly in water than in air at the same temperatures *(8)*. Whether it is due to more rapid cooling rates in water or because of hydration of the tissue has not been established. Several workers have suggested that moisture in the tissue is important and furthermore that the moisture can be broken down into "free moisture" and "bound moisture" *(1, 8, 19, 20, 21)*.

The difference between free moisture and bound moisture would be relative, depending on how much force was applied for extraction. Under a high source of energy more water could be forced from the tissue and possibly classified as free water. Bound water is electrostatically bound primarily to the minerals and various protein molecules in the tissue, but of course with unequal bond strengths. The free water would be that absorbed by the tissue and held there by secondary forces—such as dipole-dipole induction, capillary action, surface attractions, and hydrogen bonding *(19)*.

Wierbicki and Deatherage *(19)* developed a method of free water determination in raw lean beef.

Several authors have reported relationships existing between pH and acceptability of red meats *(4, 19)*. Due to post-mortem lactic acid buildup the pH naturally would decrease *(9)*, but factors affecting the variability of decrease in poultry meat have not been reported, nor have the relationships between pH and poultry meat tenderness.

A series of experiments was designed to investigate the tenderness problem further and attempt to discover why cooler temperatures and aging in water produce more rapid tenderization. Attempts were made to find out what relationships existed between pH, total and free moisture levels in the meat and tenderness. Turkeys were used in these experiments because of the larger number of samples obtainable from one carcass.

[a] Presented at Nineteenth Annual Meeting, Institute of Food Technologists, Philadelphia, Pennsylvania, May 19th, 1959.

[b] Journal paper No. 1437 of the Purdue Agricultural Experiment Station.

GENERAL PROCEDURE

Sample preparation. The turkeys used in each experiment were slaughtered by cutting the carotid artery on the left side of the neck and were allowed to bleed for 90 seconds. They were then scalded, 2 to 5 birds at a time, for 50 seconds at 140° F. (60° C.), and picked in a free-style picker for 55 seconds with tap water being sprayed over the carcasses. The carcasses were then eviscerated using as little water as possible except for washing purposes. Carcasses were distributed at random to the various aging treatments.

At the end of each aging period carcasses were removed for further evaluation. The breast was removed and the left side was cut off for studies on uncooked meat. The right side was removed and tightly wrapped in a two sheet covering of 0.0015 gauge aluminum foil and roasted for 2 hours at 325° F. (163°C.). The meat was cooled for 20 minutes at room temperature but tightly wrapped before sampling and testing for tenderness. Eviscerated weights and cooled weights were taken to calculate the water uptake or loss during aging.

Tenderness evaluation. The tenderness measurements reported are the averages of 3 samples each sheared on a Kramer shear press. Samples were 2.0 cm. by 6.6 cm. by 1 cm. in size from the *pectoralis major* muscle. Shear force values were calculated as pounds per gram of sample.

pH determination. Immediately following extraction of the whole muscle, pH was determined in vitro on the raw muscle. A 25–30 g. sample was mixed to a slurry with 50 ml. of distilled water in a Waring blender. pH was then read from a Leeds Northrup pH meter. Different amounts (25 and 100 ml.) of distilled water were tried with no effect on the pH readings.

Water determination. A rapid method for moisture determination was sought. Methods tried were lyophilization, toluene distillation, and vacuum oven drying. The method found most satisfactory for this work was toluene distillation. Between 5 and 8 g. of chopped meat were rapidly weighed on an analytical balance, placed in a distillation flask, and covered with toluene. The samples were distilled for 3 hours. Care was taken that no moisture be left in either the condenser or Bidwell-Sterling receiver by constant washing with toluene and cleansing with a rubber covered glass rod. Three samples from varying parts of the *pectoralis major* muscle were run on each carcass. The results of the 3 determinations were averaged to give a moisture determination for each muscle.

Free water determination. The method for free water determination was that of Wierbicki and Deatherage *(19)*. Immediately following the whole muscle extraction from the bird a large slice was cut from the center of the *pectoralis major*. This slice was immediately wrapped in aluminum foil and placed in a refrigerator at 35° F. for 15 minutes. Three samples (400–600 mg.) were cut from the slice, weighed on No. 1 Whatman filter paper (previously held over saturated KCl solution in a desiccator) and pressed for 1 minute at 500 p.s.i. between plexiglass plates on a Carver Press. The 3 determinations thus obtained were averaged for the carcass free water determination.

EXPERIMENTAL PROCEDURE AND RESULTS

Five experiments were conducted with slight variation in the procedures given above.

Experiment I

Procedure. Twenty-four, 13-month-old Broad White turkey hens were used in this experiment. These were divided into 2 replicates of 12 birds each. The carcasses were then subjected to 70° F. still air for approximately 45 minutes while thermocouples were placed at uniform depths of one-half inch in the breast muscles for temperature measurement. Treatments were variations in aging time and media. Two turkeys selected at random were aged for 2, 6, or 10 hours in either water or air (90% relative humidity) at 35° F. Air movement was at about 20 ft. per minute around the carcass.

Results. As might be expected there was a significant difference in tenderness between the aging times *(5, 8, 10, 12, 13, 16)*. However, no effect on tenderness was observed after any of the aging times that could be attributed to the water treatment in comparison to air. The question arose as to what effect the air at room temperature had on the carcasses before they were subjected to aging treatments. All tenderness measurements were relatively high indicating less tender meat than usually experienced.

The rate of cooling in the carcasses aged in water was much more rapid than those aged in air as would be expected. All carcasses averaged 94.5° F. before being subjected to the aging treatments. The carcasses aged in water reached 40° F. in 152 minutes and those aged in air reached 40° F. in 256 minutes. All those aged in air lost moisture; those aged in water picked up moisture. Therefore, it is difficult to conclude that differences in moisture content contributed to tenderness during the aging period.

Experiment II

Procedure. Three replications of 12, 13-month-old Broad White turkey hens were run. The carcasses were distributed at random to one of the three treatments. In the first treatment the carcasses were placed in slush ice for one hour immediately after picking. They were then eviscerated and placed back in slush ice. In the second treatment the birds were eviscerated immediately after picking and placed in slush ice. In the third treatment the birds were immediately eviscerated, held at 70° F. for one hour in air and then placed in slush ice for the remainder of the aging period. The aging periods from the time of picking until the time of cooking were 6 hours and 10 hours. At the end of the aging periods the carcasses were removed from the slush ice, drained for 3 to 4 minutes, and then weighed.

Results. Treatments administered in this experiment were due to the results obtained in Experiment I. The results of the experiment are shown in Tables 1 and 2.

As would be expected, time is again a significant tenderizing factor. Tenderness was also shown to be affected significantly by the aging treatments. In Table 2 it can be seen that the average tenderness scores for treatments 1 and 2 are nearly equal, whereas the average score for treatment 3 is considerably higher. This indicated that holding the carcass in air before immersion in slush ice caused the meat to be less tender even after the 10 hours of aging. The average amount of water uptake per bird for treatments 2 and 3 were very similar, being 4.1 and 3.7%, respectively. In treatment 1, however, the average water uptake per bird was 5.9%. Since the average tenderness scores were nearly equal in treatments 1 and 2, the effect of water uptake as a tenderizing mechanism is not clearly shown here. During the period when the carcasses of treatment 3 were held in air before immersion in slush ice the average moisture loss per bird was .94% by dehydration. This might give some insight into the cause for the less tender birds.

TABLE 1

An analysis of variance, Experiment II, in which mature turkeys were given three aging treatments to determine the effect of moisture on tenderness

Source of variance	d.f.	ss.	m.s.	F values
Time of aging	1	521.36	521.36	22.82
Treatments	2	518.48	259.24	11.35
Replications	2	520.47	260.24	11.39
Time × treatment	2	37.50	18.75	.82
Time × treat. × reps.	4	475.71	118.93	5.20
Treat. × reps.	4	125.56	31.39	1.37
Time × reps.	2	182.24	91.12	3.99
Error	18	411.25	22.12	
Total sum of squares	35	2792.57		

F values needed for significance *(17)*:

d.f.	0.1 level of probability	.05 level of probability
1,18	8.28	4.41
2,18	6.01	3.55
4,18	4.58	2.93

TABLE 2

Average tenderness scores for treatments, Experiment II

Aging times	Scores	Treatments	Scores	Replications	Scores
6 hours	27.20	Treatment 1	20.72	Rep 1	25.13
10 hours	19.54	Treatment 2	20.62	Rep 2	18.07
		Treatment 3	28.72	Rep 3	26.86

Experiment III

Procedure. Twenty, 15-month-old Broad Breasted Bronze female turkeys were used in this experiment. These were slaughtered, scalded, and picked as in Experiment I. After picking, the carcasses were placed in slush ice, eviscerated, weighed, and then placed back in slush ice for aging periods of 0, 2, 5, 8, and 12 hours, and then weighed again. The carcasses tested without aging were tested within 10 minutes after picking. After the aging period the right side of the breast was removed for pH and water determinations. The remaining portion of the breast was roasted in aluminum foil for 3 hours at 310° F. in a reel-type oven. Four replications of 5 birds each were run.

Results. The results of this experiment are shown in Tables 3 and 4.

TABLE 3

Averages of raw data, Experiment III, in which 20 mature turkeys were aged in water at 32° F. for 0, 2, 5, 8, and 12 hours

Hours aged	pH	Tenderness	% H_2O uptake	Av. % H_2O	Av. % Free H_2O
0	6.40	60.2	0	73.2	35.6
2	6.19	46.7	3.2	73.7	42.8
5	5.95	28.1	4.4	73.2	44.5
8	5.89	22.2	5.6	73.5	43.4
12	5.89	17.2	5.9	73.2	43.6

TABLE 4

Relationships between tenderness, pH, and % free water in mature hen turkeys aged for 0, 2, 5, 8, and 12 hours post-mortem in water—calculated on individual bird scores

Combinations	Degrees of freedom	r value
Tenderness × pH	18	.8214**
Tenderness × % free water	18	−.4367
pH × % free water	18	−.6956**

** Significance at .01 level of probability *(17)*.

Experiment IV

Procedure. This experiment was conducted on 15, 15-month-old male Broad Breasted Bronze turkeys. Three replications were run on 5 birds each in which carcasses were aged uncovered in air at 35° F. for 0, 2, 5, 8, and 12 hours.

Results. The results of Experiment IV are shown in Tables 5 and 6.

Experiment V

Procedure. Thirty-six, 18-week-old Broad White turkeys were used in this experiment. The experiment was divided into 3 replications of 12 birds each. Within each replication birds

TABLE 5

Averages of raw data, Experiment IV, in which 15 mature tom turkeys were aged in air at 32° F. for 0, 2, 5, 8, and 12 hours

Hours aged	pH	Tenderness	% H_2O loss	Av. % H_2O	Av. % Free H_2O
0	6.40	56.5	0	73.8	31.4
2	6.20	49.1	2.0	74.5	36.9
5	5.83	32.8	1.9	75.1	37.4
8	5.87	21.0	1.9	74.3	39.8
12	5.83	22.4	1.9	74.7	40.7

TABLE 6

Relationships between tenderness, pH, and % free water in mature turkey toms aged in air at 35° F. for periods of 0, 2, 5, 8, and 12 hours—calculated on individual bird scores

Combinations	Degrees of freedom	r values
Tenderness × pH	13	.7058**
pH × % free water	13	—.4425
Tenderness × % free water	13	—.0619

**Significance at .01 level of probability *(17)*.

were assigned at random to water and air treatments, aging periods, and testing treatments (i.e. first or second tested within aging time, left or right side of breast cooked for tenderness measurement). In each replication one bird was aged in slush ice at 32° F. and one bird was wrapped in polyethylene and aged at 32° F. in air for each of the assigned aging periods of 2, 5, 8, 12, and 16 hours. Within each replication two birds were tested with no aging treatment.

Results. The results of Experiment V are shown in Tables 7, 8, and 9.

TABLE 7

Combined averages of raw data, Experiment V, in which 36 young turkeys were aged in air (packaged) and water at 32° F. (0° C.) for periods of 0, 2, 5, 8, 12, and 16 hours post-mortem

Treatment		pH	Tenderness	% total H_2O	% free H_2O	% H_2O change
Condition	Time hours					
Air	0	6.3	33.5	70.6	34.5	0
Water	0	6.2	43.9	70.0	38.3	0
Air	2	6.1	30.0	74.1	32.3	—0.5
Water	2	6.1	33.7	73.4	37.7	3.7
Air	5	5.8	15.8	71.9	42.6	—1.6
Water	5	5.9	16.9	72.3	39.3	3.0
Air	8	5.8	16.5	73.2	34.0	—0.8
Water	8	5.9	17.5	74.2	39.5	5.7
Air	12	5.8	15.2	71.2	41.6	—0.8
Water	12	5.8	15.7	72.2	49.1	6.6
Air	16	5.9	11.1	71.5	35.9	—1.0
Water	16	5.9	12.5	71.7	40.0	6.8

DISCUSSION

The results of the first two experiments indicate that the more rapid tenderization found by aging in water can be attributed neither to water uptake nor cooking rates. These results were borne out again in Experiment V when the packaged carcasses aged in air tenderized more rapidly than unpackaged carcasses aged in water, even though there were gross differences between water uptake and loss between the two treatments. Moreover, the tenderizing effect produced by aging in water appears to be largely due to the prevention of dehydration on the hot carcass. As is shown in Tables 5 and 7 the dehydration is greater in the early periods of aging and is apparently followed by a rehydration. However, this rehydration seemingly does not correct the damage done by the dehydration as the toughening effect is observed after 10 hours of aging. It should be remembered that these were mature, well finished turkeys. In younger birds or carcasses with less finish the effect would probably be more pronounced.

In Experiments III, IV and V the only consistent result produced was that early post-mortem tenderization was closely associated with pH. The correlation coefficients are high enough in these instances to suggest a fairly strong relationship. Certainly, one would expect the pH to decrease with time after slaughter

TABLE 8

Relationships[1] between pH, per cent free water, per cent total water, and tenderness, Experiment V

Combinations	Degrees of freedom	r values
Whole test averages		
Tenderness scores × pH	10	.8927**
Tenderness scores × % total H_2O	10	—.2359
Tenderness scores × % free H_2O	10	—.3698
pH × % free H_2O	10	—.4550
Individual scores		
Tenderness scores × pH	34	.8209**
Tenderness scores × % total H_2O	34	—.2138
Tenderness scores × % free H_2O	34	—.2640
pH × % free H_2O	34	—.4206*

[1] Figures are for relationships found using both individual scores and averages for the whole test.

**Significance at .01 level of probability *(17)*.

*Significance at .05 level of probability.

(9), and also the tenderness to increase. The close association, however, could suggest a simple explanation to more rapid tenderization at lower temperatures. The pH decrease is due to post-mortem glycolysis producing a build up of lactic acid in the tissue. Glycolysis is an exothermic reaction *(9)*, and therefore if the by-product heat could be dissipated more

TABLE 9

Analysis of variance on tenderness scores, Experiment V

Source of variance	d.f.	ss.	m.s.	f. value
Time	5	3483.2	696.6	4.65**
Water vs. air	1	82.8	82.8	.55
Replications	2	29.7	14.9	.10
Times × water vs. air	5	78.4	15.7	.10
Error	22	3296.1	149.8	
Total sum of squares	35	6970.2		

**Denotes significance at .01 level of probability *(17)*.

rapidly from the tissue, the glycolysis should be more complete. The reason that this temperature reaction has not been found in beef might possibly be that most tests on beef have not been initiated soon enough after slaughter to pick it up *(4, 6, 14, 22)*.

The close association of pH and early post-mortem tenderness suggests that glycolysis is an integral part of early post-mortem tenderization. This would substantiate the findings of some workers in the field of red-meats *(2, 3, 4)*, and helps tie together many theoretical considerations given to the tenderness problem—such as ATP depletion and protein alterations *(2, 3, 7, 9, 11, 14, 18, 20)*.

As can be seen from the results of Experiments III, IV, and V the per cent free water in the tissue, and

the per cent total water in the tissue (within the experimental considerations) had little effect on tenderization during the period studied. The amount of free water in the tissue was greater for the birds aged in water than those aged in air, with one exception, even though the tenderness was not apparently affected by these differences. Possibly at longer aging times the per cent free water in the tissue would prove to exert some influence on tenderness, but this influence would be expected to be small.

As can be seen in Experiments III and V the water uptake was not shown in the moisture analysis of the meat indicating that most of the moisture is absorbed by the skin and fatty layers under the skin of the turkey carcass.

SUMMARY

Five experiments were conducted on turkeys to study the relationships between moisture levels in the meat, per cent free moisture in the meat, cooling rates, water uptake, pH, and post-mortem tenderness.

Water uptake and rates of cooling were not shown to affect tenderness, whereas dehydration on hot carcasses was found to produce a toughening effect which could not be aged out of the meat. Tenderization during early post-mortem periods was found to be closely associated with pH. Total moisture content of the tissue did not appear to be associated with water uptake, nor was it shown to be related with tenderness. Per cent free moisture in the meat was found to be associated with pH in one instance, but for the post-mortem period studied it did not appear to be related to tenderness.

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Anthocyanase Activity and Its Possible Relation to Scald in Sour Cherries[a, b]

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(Manuscript received May 21, 1959)

SCALD OF SOUR CHERRIES *(Prunus cerasus)* has been shown to be caused by a combination of bruising and time-temperature effects related to picking, transportation, and other pre-processing conditions *(8)*. This phenomenon is characterized by a migration of the red anthocyanin pigment from the skin into the flesh of the fruit, followed in turn by the loss of the pigment and the appearance of a brown discoloration.

As pointed out by LaBelle *(8)* it is important to differentiate between scald and the subsequent browning of cherries. The latter is believed to be the result of an enzymatic oxidation, which normally follows disruption of cellular structure, whereas scalding is typified by a loss of anthocyanin whether browning occurs or not.

Enzymes capable of destroying anthocyanins have been found in fungi *(4, 5, 6)* and in higher plants *(2, 10)*. The fungal anthocyanase, now commercially available, has found application in the removal of unwanted excessive amounts of anthocyanins in such products as blackberry wine, and blackberry jams and jellies *(12)*.

This report is concerned with an enzyme system in sour cherries capable of causing the destruction of anthocyanins and a consideration of some of its properties. The anthocyanase activity of several varieties of sweet cherries and of several types of berries was determined at various stages of maturity.

MATERIALS AND METHODS

The various fruits used in this study were obtained from the Experiment Station orchards and farms. These were employed both as fresh fruit and following frozen storage at −18° C. Crude anthocyanase preparations were made from fresh or frozen fruit as follows. The fruit was destemmed and washed, the flesh sliced away from the pits (if any), and 10 to 25 g. samples homogenized with four times the weight of cold distilled water in a chilled Waring blender. The blending was stopped after 30 seconds and particles adhering to the walls of the blender were scraped down into the liquid. Blending was then continued for an additional 90 seconds.

The activity of the enzyme was determined in a manner similar to that used by Bayer and Wegman *(2)* in studying Coleus cyanin oxidase. The method consists of adding the enzyme suspension to 1 ml. of citrate-phosphate buffer (M citric acid adjusted to pH 5.8 with M K_2HPO_4), 0.3 ml. of 0.1M catechol, 1 ml. of anthocyanin in 0.01 N HCl and sufficient water to make a total of 3 ml. A 0.5 ml. aliquot was withdrawn immediately after adding the enzyme and pipetted into 5 ml. of N HCl. The rest of the mixture was incubated with slow shaking on a Dubnoff shaker at 30° C. and aliquots transferred into 5 ml. of N HCl after suitable times. The optical density (OD) at 510 mμ was then determined for each sample using a Bausch and Lomb Spectronic 20 photometer, and the loss in light absorption used as a measure of relative enzyme activity.

Dry weights were determined by allowing 10 ml. of homogenate to air dry in tared Petri dishes, followed by desiccation over P_2O_5 to constant weight.

The anthocyanin substrate was antirrhinin, prepared from sour cherries by the method of Li and Wagenknecht *(9)*. The antirrhinin concentration was adjusted so that the unreacted control flasks had an OD at 510 mμ of 0.75 when diluted with 10 volumes of N HCl.

Studies on oxygen consumption were made in the Warburg respirometer at 30° C. All flasks contained 1 ml. phosphate-citrate buffer, pH 5.7, 1 ml. anthocyanin in 0.01 N HCl, and water plus various additives to make a total volume of 4.2 ml. The center well contained 0.2 ml. of 20% KOH to absorb CO_2.

Sour cherry anthocyanase was partially purified as follows: 75 g. of anhydrous ammonium sulfate was added to 150 ml. of press juice (prepared from frozen pitted cherries) and allowed to stand for several hours at 4° C. The mixture was centrifuged for 15 minutes at 2000 r.p.m., the supernatant liquid decanted and discarded. The precipitate, when taken up in 20 ml. distilled water, gave a cloudy suspension. Therefore, the mixture was centrifuged as before and the precipitate was resuspended in 20 ml. distilled water and used as such.

For purposes of comparing the relative anthocyanase activity of the various fruits and berries used in this study, a unit of anthocyanase was defined as the amount of enzyme which caused a change of 0.01 units of OD at 510 mμ in 5 minutes at 30° C. The relative activity was expressed in activity units per 100 mg. dry weight.

Glucose oxidase, obtained from Worthington Biochemical Corporation (Freehold, N. J.), was capable of consuming 400 μl. O_2 per hr. per mg. *(3)*. While it had a Kat f of 17.8, it allowed the accumulation of enough H_2O_2 to support the oxidation of guaiacol as catalyzed by cabbage peroxidase.

RESULTS

It has been found that extracts of sour cherries *(Prunus cerasus,* var. Montmorency*)* can cause the enzymatic decomposition of anthocyanins. Anthocyanase activity has been demonstrated in press juice of fresh fruit and also in homogenates and acetone powders prepared from fresh or frozen cherries. The pH optimum in phosphate-citrate buffer was shown to be in the range of pH 5.7 to 6.0 in agreement with that shown for Coleus cyanin oxidase *(2)*.

Catechol enhances the activity of sour cherry anthocyanase, nearly doubling the enzymatic activity of homogenates prepared from fresh cherries. The need for added catechol became greater as the enzyme system was purified by means of ammonium sulfate precipitation, Table 1.

Catechol at a concentration of 0.01 M was found to be most effective in enhancing anthocyanase activity of press juice enzyme preparations. Higher or lower concentrations resulted in lower enzyme activity, Table 2.

[a] Presented at the Philadelphia Meeting of the Institute of Food Technologists, May 18, 1959.

[b] Approved by the Director of the New York State Agricultural Experiment Station for publication as Journal Paper No. 1181.

TABLE 1

Effect of added catechol on sour cherry anthocyanase activity

	Change in OD at 510 mμ in 5 min.
Cherry press juice, 0.2 ml.	
Catechol, 0.007M	0.44
No added catechol	0.25
Purified enzyme, 0.2 ml.	
Catechol, 0.007M	0.19
No added catechol	0.02

Hydrogen peroxide can bring about destruction of anthocyanins *(11)*. This nonenzymatic destruction by H_2O_2 was demonstrated using purified sour cherry anthocyanins. It was considered possible that catechol functioned by providing H_2O_2 through an oxidative process. In order to test this possibility, the glucose-glucose oxidase system *(3)*, which consumes oxygen and produces H_2O_2, was employed as a continuous source of low concentration levels of H_2O_2, similar to those which might be provided by catechol oxidation. Overall oxygen uptake was compared with anthocyanin destruction during an incubation period of 45 minutes using Warburg respirometers, Table 3. The results indicated that while the glucose-glucose oxidase system did cause some increase in decolorization of anthocyanin, the extent was much less than that seen when only catechol and cherry anthocyanase were present. In fact, the effect was

TABLE 2

Optimum catechol concentration for enhancing sour cherry anthocyanase activity

Concentration of catechol in reaction mixture, M	Change in OD at 510 mμ in 5 min.
0	0.25
0.0017	0.34
0.007	0.44
0.01	0.51
0.017	0.37
0.023	0.30
0.033	0.22

Cherry press juice, 0.2 ml. per flask.

nearly additive. The oxygen consumption obtained with the glucose oxidase system may not reflect a stoichiometric accumulation of H_2O_2, since the glucose oxidase contained some catalase. However, there was sufficient H_2O_2 accumulated by this system to support the enzymatic oxidation of guaiacol by cabbage peroxidase. The role of catechol remains obscure at present. It cannot be replaced by reducing substances such as ascorbic acid, ferrous iron, cysteine or bisulfite.

The anthocyanase of sour cherries requires oxygen for activity. Experiments using Thunberg tubes showed that no decolorization took place under the assay conditions in the absence of air, Table 4. Furthermore, the need for oxygen is connected with an enzymatic step, since reaction mixtures unchanged during vacuum incubation, when heated for five minutes in a boiling water bath followed by incubation in air did not produce a decrease in color. There was no regeneration of red color by heating with acid following enzymatic decoloriza-

TABLE 3

Effect of exogenous H_2O_2 on activation of sour cherry anthocyanase by catechol

	Change in OD at 510 mμ in 45 min.	O_2 uptake, μl. in 45 min.
Sour cherry anthocyanase (SCA)	0.09	0
SCA + catechol	0.23	30
SCA + glucose oxidase + glucose	0.09	77
SCA + glucose oxidase + glucose + catechol	0.27	97
Glucose oxidase + glucose	0.05	70

Catechol, 0.01M; glucose oxidase, 0.15 mg.; SCA, 0.8 ml. purified enzyme; glucose, 0.083M.

tion of the anthocyanins. These properties seemed to differentiate the mechanism of action of the cherry anthocyanase from that of fungal anthocyanase described by Huang *(4)*.

The marked similarity of the sour cherry anthocyanase to the Coleus enzyme extended to the fact that thiourea is an inhibitor of both enzymes. The decrease in OD in 25 minutes was 0.08 in the presence of 0.04 M thiourea, compared with a decrease in OD of 0.25 in the control.

The anthocyanase content of several varieties of sweet cherries, yellow-fleshed and red-fleshed sour cherries, and of black raspberries, blackberries and blueberries was examined at several stages of maturity during the 1958 season. These samples included green, partially colored, ripe and overripe fruits, Table 5. Anthocyanase activity was observed in all of the cherry varieties examined at all stages of maturity. The

TABLE 4

Oxygen requirement of sour cherry anthocyanase

Conditions	Change in OD at 510 mμ in 30 min.
1. Incubated in air	0.19
2. Incubated *in vacuo*	0.02
Sample from step 2, heated 5 min. at 100° C., then	
3. Incubated in air	0.01
4. Incubated *in vacuo*	0.01

Purified enzyme, 1 ml. per flask.

highest levels of enzyme activity were present in the green unripe fruit and diminished with increasing maturity.

Anthocyanase activity was shown to be present in the 3 types of berries employed in this study. Blueberries contained relatively large amounts of anthocyanase, blackberries showed moderate amounts of the enzyme, and black raspberries possessed very weak activity.

DISCUSSION

The color of sour cherries constitutes an important quality factor, readily evaluated by the consumer, and thus has a significant influence upon the value of the product. In sour cherries loss of red color directly involves the anthocyanin pigments which have been shown to be cyanidin-3-rhamnoglucoside and cyanidin-3-diglucoside *(9)*. Pigments such as these are readily oxidized or reduced with a loss in red color. A secondary source of red color loss may lie in the masking of red pigment by miscellaneous brown products developing in the fruit.

Sondheimer and Kertesz *(11)* have reported the oxidation of pelargonidin-3-glucoside by hydrogen peroxide, and Huang *(4)* presented data suggesting an oxidation of cyanidin or its derivatives to colorless compounds. Results with model systems have paralleled observations made on the original fruit products. However, the exact chemical nature of the products of anthocyanin breakdown has not been established.

Bate-Smith *(1)* has shown that many plants contain compounds, which when treated with acid, are transformed into colored cyanidin derivatives. Other workers, as King and Clark-Lewis *(7)*, have demonstrated that acid will convert flavan compounds into cyanidin derivatives. The possibility exists that a reversal of such a reaction, with cyanidin forming colorless flavans, may contribute to pigment losses in fruit.

The situation as it appears at the present time is that pigment loss prior to heat processing may be

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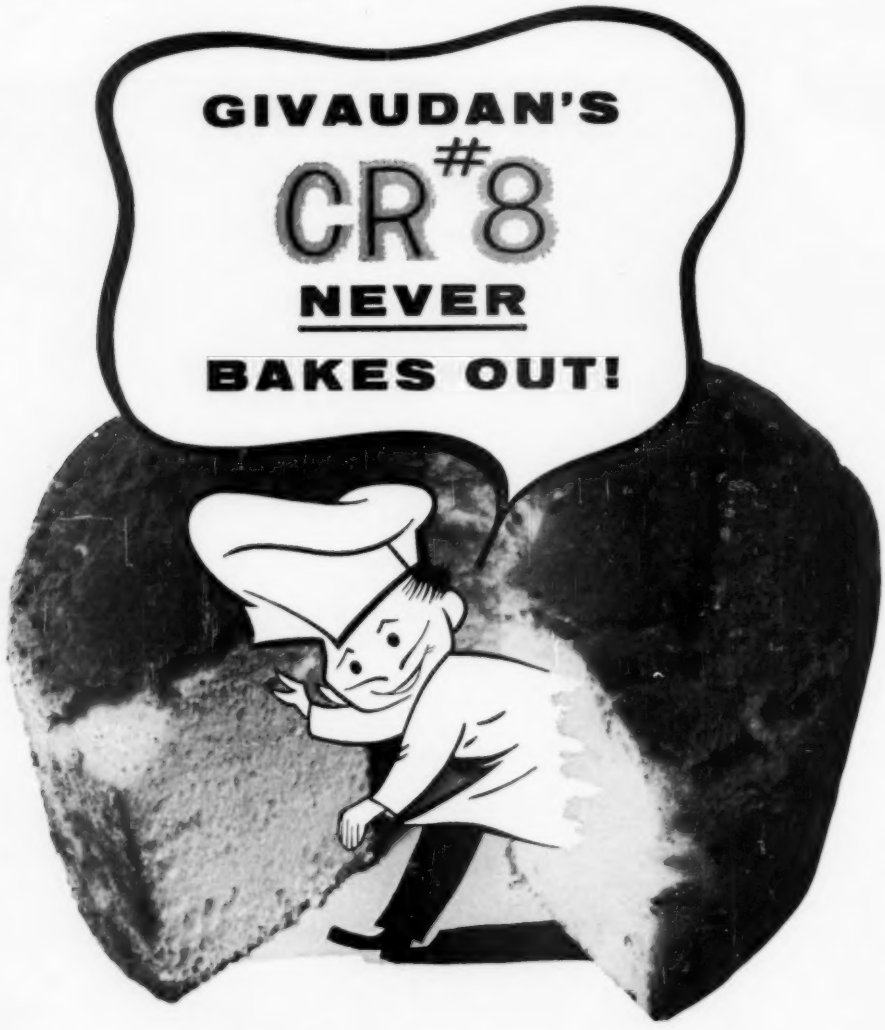

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TABLE 5

Changes in anthocyanase activities of several fruits with increasing maturity

Sample	Anthocyanase activity, units per 100 mg. dry weight			
	Green	Ripe	Post-harvest	Pre-harvest
Sweet cherries (*Prunus avium*), var.				
Windsor	448	196	.....	286
Bing	263	158	.....	224
Yellow Glass	320	208	.....	250
Sour cherries (*Prunus cerasus*), var.				
Montmorency	290	140	120	220
English Morello	274	124	146	262
Cherries (*Prunus avium* × *Prunus cerasus*), var.				
Royal Duke	354	172	.....	258
Black raspberries (*Rubus occidentalis* L.), var.				
Dundee	48	0	0	0
Blackberries (Rubus spp.)				
Mixed varieties	96	306	186	32
Blueberries (*Vaccinium corymbosum* L.), var.				
Rubel	236	284	.....	262

enzyme catalyzed, spontaneous, or a combination of these two types of reactions.

Sour cherries in a scalded condition are definitely liable to lose anthocyanin by both of these mechanisms. The bruising, which is associated with scald, causes disruption of the cells of the anthocyanin-containing peel. If the bruising is quite extensive, the cells of the fruit beneath the peel will also be disrupted, allowing for contact between anthocyanase and its substrate. These changes can be followed visibly if cherries showing incipient scald are peeled at various times after the first symptoms of scald are noted. Initially the area immediately under the scald area of the skin shows a pink coloration. In later samplings the pink color will have disappeared, and in terminal samples oxidative browning will have begun.

Were it not for the physical barrier between enzyme and substrate which actually prevents pigment loss in intact fruits, one might have been led to expect that the more heavily pigmented Windsor, Bing, and Royal Duke cherries, as well as the red-fleshed English Morello might contain very little anthocyanase activity, or none at all. By this argument, Yellow Glass might have been expected to be high in anthocyanase activity.

This study has shown that anthocyanase activity is not restricted to sour cherries, for all of the varieties of cherries examined, including the sweet cherries, produced relatively active preparations at all stages of maturity. It is of interest to note that anthocyanase activity was readily demonstrable in such highly pigmented fruits as blackberries, as well as in blueberries, where the pigment is confined to the outer skin.

Whereas anthocyanase is most probably involved in the destruction of anthocyanin pigment in the early stages of sour cherry scald, no function can be ascribed to this enzyme system in intact fruits at the present time. The activation of the enzyme by catechol remains unexplained at present. That it may be replacing naturally occurring phenolic compounds of the cherry was suggested by the fact that the catechol requirement of the enzyme increased with purification of sour cherry anthocyanase.

SUMMARY

Anthocyanase is believed to participate in the early stages of scald in red sour cherries through destruction of anthocyanin pigments.

Sour cherry anthocyanase was prepared from homogenates of fresh fruit and partially purified from press juice by ammonium sulfate precipitation. The enzyme has limited solubility in water and exhibits maximum activity at pH 5.7 to 6.0.

The enzymatic activity of a homogenate of fresh cherries was nearly doubled by the addition of catechol. Purified enzyme preparations were nearly inactive unless catechol was added. The optimum concentration of catechol was 0.01M.

The anthocyanase of sour cherries requires the participation of oxygen for activity and was inhibited by thiourea.

Sour cherry anthocyanase is quite similar in its properties to Coleus cyanin oxidase, and is dissimilar to fungal anthocyanase.

The presence of anthocyanase has also been demonstrated in sweet cherries, black raspberries, blackberries and blueberries. The amount of enzyme activity in these fruits at several stages of maturity has been studied.

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Pregelatinized Starches for the Food Processor[a]

(Manuscript received May 21, 1959)

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WITH THE SWIFTLY developing lines of powdered beverages, cake mixes, dried soups, salad dressings, and sauces, pudding and dessert mixes, etc., being greeted by unprecedented consumer and institutional acceptance, there has been a growing need for ingredients specifically suited for the processing and final preparation of these convenience products. Controlled thickening and stabilization as a function of the ingredients become especially important in these modern food items, where the main selling point is ease of preparation, without the need for precise cooking techniques.

One of the basic stabilizers gaining in importance in convenience foods are the pregelatinized starches, which eliminate the need for elaborate cook-up procedure by either the processor or consumer *(1)*. Drum-dried cold-swelling starches are not new. They have been available primarily for industrial uses for at least 25 years *(2)*. However, it was not until this decade's trend to the convenience products mentioned that pregelatinized starches were developed and used successfully in one specific food—instant puddings. At that time the relatively undeveloped state of pregelatinized starches allowed only limited usage of these ingredients in convenience foods. One drawback was their instability under certain pH conditions. As a result, the food processor often found it necessary to use other thickeners and stabilizers, such as Irish moss, water-soluble gums, etc., to provide the base for convenience products. However, these ingredients, in turn, also presented several drawbacks, such as high price, poor dispersion qualities, the effect of metallic ions present in the product, unacceptable taste and flavors, etc. Pregelatinized starches have made significant strides in the past 10 years as a result of the advances of starch technology and research in modifying and processing pregelatinized starches to extend their uses in a much wider variety of food applications.

A pregelatinized starch is produced by cooking and drying the starch dispersion on heated rolls or drums. This process involves feeding a starch slurry (after completion of processing, refining, and blending with other starches, sugars, etc.) on the outer surface of a steam-heated revolving drum. The rate of rotation of the drum is set so that the material is dried and scraped off by a doctor blade when the drum reaches a certain position. The operation can be performed on single or double drums, with the latter providing greater capacity. This pre-cooking process swells the starch granules and thus conditions them to thicken and gelatinize in cold liquids, without need for subsequent heating. Thus, the starch manufacturer is doing the actual starch cooking operation in his own plant. By this method, gelatinization time, gel texture, stability and composition can be engineered into the starch according to the requirements of the food manufacturer's equipment and the food product involved. Product uniformity from item to item and batch to batch is assured and the user is relieved of the costly cook-up and gelatinization control operations necessary with ordinary starches.

Unfortunately, there is a dearth of literature (except for patent claims) on pregelatinized starch use and application. This paper will endeavor to outline some of the advances made in the starch technology field in recent years and provide suggestions on how a food processor can take advantage of the properties of pre-cooked starches through proper examination, control, and intelligent application.

EXPERIMENTAL

Using a Brookfield viscosimeter Model RVF with helipath stand,[b] viscosities of a group of pregelatinized starches were measured at varying concentrations.

For any one determination, the procedure was: The pregelatinized starch was weighed on a dry basis, then added very slowly into 300 ml. of distilled water at 25° C. in a wide-mouth glass pint jar under constant agitation. After addition of the starch, the agitation was stopped and the jar filled to the 400 ml. mark. Agitation at high speed was then resumed for 10 minutes more, and the solution was then allowed to set for 1 hour. A Brookfield viscosity reading was taken after 7 turns of the spindle were completed in the solution. The spindle and gear speed was chosen so that the reading on the Brookfield dial came as near the dial center as possible. Another Brookfield reading was made under the same conditions after the jar had set for 3 hours at 25° C.

The same stirring equipment—stirrer, propeller, glass jar—was used for all determinations. It is emphasized that these measurements are of relative viscosities, valuable for comparing starches and evaluating intended applications in a food product.

Our results were obtained with a laboratory stirrer similar to the standard Fischer model stirring apparatus (Fischer Catalog No. 14-498) with a variable-speed direct-worm drive. The stainless steel stirrer was a simple 4-blade propeller on an 8-in. shaft.

Results of these determinations provide a curve of relative starch viscosity at 25° C. versus the concentration in aqueous solution. For further controls, the following analyses of a pre-cooked starch may be made according to standard procedures: moisture, pH of a 2% solution, ash, color, mesh, thermophiles, and, if required, a storage stability test on a modified Swift Tester.

Based on the analytical results, specifications may then be drawn up by the food manufacturer for use by the quality control laboratory. It should be emphasized that tolerances of ± 10% on the viscosity results should be allowed because of the

[a] Presented at the Nineteenth Annual Meeting of the Institute of Food Technologists, Philadelphia, May 17, 1959.

[b] Brookfield Engineering Laboratories, Inc., Stoughton, Mass.

natural differences in raw materials, starch processing steps, and the method of control which usually is relative rather than absolute in measurement. An increase in viscosity after three hours standing at 25° C. will indicate the amount and type of retrogradation of the starch solution.

A "use" test *(3)* should also be made at the same time by the quality control laboratory to supplement the results obtained by the other suggested tests.

RESULTS AND DISCUSSION

Figure 1 illustrates viscosity curves versus concentrations of a number of pregelatinized starches differing either by type of starch base or processing method.

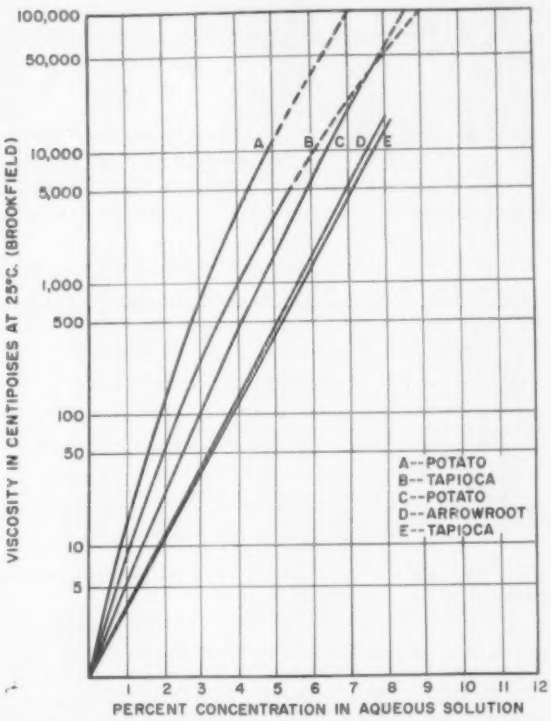

Figure 1. Comparative viscosities of pregelatinized starches in aqueous solution.

Referring to such a series of curves and other analytical results will help the food processor evaluate the usefulness of a particular starch—regardless of source—in his product. The usual supplementary information is provided in a typical specification chart (Table 1).

For example, if Starch E in Figure 1 is used at present in an instant pudding mix, and reasons of economy cause the processor to consider changing to a higher viscosity starch, a glance at this viscosity versus concentration curves will indicate that Starch A may yield the same viscosity at a lower load-level use. On the other hand, the new starch may involve product textural changes as indicated by the three-hour lapse-time viscosity, and as a result he may not be able to use this replacement. However, if this change in texture and viscosity is not detrimental to his product, he may then be able to substitute Starch A for Starch E at considerable savings in the cost of his packaged mix.

TABLE 1

Pregelatinized starch B product information and specifications

Moisture	8.0% (max.)	
Color	White	
Mesh	Over 100	0.40%
	Over 140	0.90
	Over 200	5.60
	Through 200	93.10
pH (2% sol)	6.05	
Ash	0.15%	

Viscosity at 25° C.* (Brookfield)

Per cent concentration	Viscosity (cps)	
	1 hr. stand	3 hr. stand
1	8	10
3	248	320
5	2800	3500
8	gel (approx. 40,000)	gel (approx. 50,000)

Physical characteristics (5% sol)

Appearance	Translucent
Taste	Smooth
Texture	Acceptable
Storage stability (activated O_2 test)	2 years plus
Thermophiles	Nil
Base	Tapioca

* Starch dispersed in distilled water (25° C.) with mechanical stirrer for 10 min.

APPLICATION

Pregelatinized starches, as noted before, were originally used for the most part in the pudding and dessert field. A typical formulation for an instant type of pudding is noted in Table 2, where the formulation utilizes the characteristics of Starch E. This recipe involves a milk-gel system, so the starch should have a relatively low viscosity and low gel action to allow the pudding to retain its even texture for a relatively long time. Starches C and D are also used in instant puddings, with their application dependent on the type and amounts of phosphate salts used in the processor's milk-gel system. Since each manufacturer usually employs a different mix formulation, he requires a specific pre-cooked starch.

One of the most important properties of Starch E in an instant pudding is the fact that it is based on tapioca, which has the property of extreme blandness that enhances the flavor and taste of the pudding. But Starch E lacks stability in acid solutions and can be used only under neutral pH conditions. Hence recent developments in starch processing have endeavored to overcome this detriment, and Starch B evolved, as a result. This new product is a tapioca-based starch, as is Starch E, but Starch B has a higher

TABLE 2

Formulation of instant pudding mix using pregelatinized starch

Chocolate instant pudding		
Ingredients	Lbs.	Oz.
Starch E	20	....
Cocoa powder	13	....
Sugar (4X)	26	....
Vanillin (+ flavors)	To taste	To taste
Phosphate salt mix*	....	19

*Tetrasodium pyrophosphate anhyd., 12 oz. Disodium orthophosphate anhyd., 7 oz.

gel character as shown by viscosity evaluations. Furthermore, it has considerable resistance to acidic pH conditions which allows the food processor to utilize Starch B as a basis for example in cold-water-soluble fruit-pie formulations and fountain-ade mixes. Typical formulations are shown in Table 3. This starch, when used by the pie baker and food processor, eliminates the need for cooking apparatus with high upkeep and labor costs, valuable floor space, and it requires the least elaborate equipment for preparation. As a further economic advantage, only a minimum

TABLE 3

Formulation of food products using pregelatinized starches

Cherry pie filling		
Ingredients	Lbs.	Oz.
Sugar	7	....
Starch B	1	6
Salt	....	2
Water	6	....
One 30 lb. can 5 + 1 frozen cherries		

Crushed pineapple fountain-ade (Fruit topping)		
Ingredients	Lbs.	Oz.
Sugar	60	....
Starch B	6	....
Salt	....	5
Water (+ juice)	83	....
Crushed pineapple	60	....

amount of additive flavor is required in food products such as fruit pie fillings, toppings and fruit fountain-ades because the starch is based on tapioca. Furthermore, it eliminates time-consuming cook-up procedures with resultant evaporation losses, costly clean-up requirements and long periods of cooling and refrigeration costs. Pregelatinized starches are also available with other specialized properties such as freeze-thaw stability in aqueous dispersions.

Since a pie is baked and eaten in a relatively short time, there is no need for an added preservative. On the other hand, a fountain-ade requires a preservative such as sodium benzoate to increase storage stability. The fountain-ade recipe shown in Table 3 eliminates the usual sugar-syrup cooking procedures and allows the food processor to develop new ideas for such products because of simple make-up procedure.

Our laboratories have applied the other starches shown in Figure 1 to a number of food products. Formulations for a chiffon pie filling and a stabilized meringue are shown in Table 4 based on Starches D and B, respectively, because of the textures and viscosities required by the products.

Table 5 contains the formulations for a simple icing mix and an instant lemon pie filling mix. Starch D was used in the icing base because it helps prevent syneresis whereas Starch B was applied in the lemon pie filling to provide the gel action necessary for a stable product.

A few special techniques will facilitate the application of pregelatinized starches in food products. For example, the pre-cooked starch should be thoroughly blended with the other dry materials before mixing with liquids. This procedure provides easy dispersion. A particular formulation may require dumping of the total dry blend into the liquid rather than slow addition. The method, of course, depends on the specifications and requirements set up by the food processor and starch manufacturer.

TABLE 4

Formulations of food products using pregelatinized starches

Instant chiffon pie filling		Instant meringue mix	
Ingredients	Lbs.	Ingredients	Lbs.
Sugar	65	Egg albumen (pdr.)	65
Starch D	20	Sugar	10
Gelatin (200 Bloom)	6	Starch B	20
Whipping agent	5	Citric acid	¼
Phosphate salt mix*	1¼	Flavor	To taste
Salt	1		
Citric acid	1		
Lemon juice (pdr.)	1¼		
Color & flavor	To taste		

* Tetrasodium pyrophosphate anhyd., 1 lb. Disodium orthophosphate anhyd., ¼ lb.

Granulation and mesh size are important factors to consider both from a recipe make-up procedure and package requirements of the finished food product. Flavor, taste, odor, texture and uniformity are also

TABLE 5

Formulations of food products using pregelatinized starches

A. Instant icing mix		B. Instant lemon pie filling	
Ingredients	Lbs.	Ingredients	Lbs.
Sugar (6X)	100	Sugar	10
Starch D	6	Starch B.	2
Dry milk pdr.	5	Lemon juice (pdr.)	1¼
Dextrose	3	Citric acid (pdr.)	1/10
Salt	¾	Salt	1/10
Shortening	15	Water	20
		Butter or oleo (melted)	1
		Lemon oil, color	To taste

important properties when a specific pregelatinized starch is applied to a food item.

It has been shown that today's increased variety of specialized pregelatinized starches can enjoy a wide list of food applications. Table 6 shows a number of food products where starches have been successfully used as base thickeners and stabilizers with subsequent advantages of economy and convenience.

CONCLUSION

Pregelatinized starches are growing in numbers and types because of advances in the field of starch tech-

TABLE 6

Check chart of pregelatinized starch uses

Food use	Pregelatinized starch				
	A	B	C	D	E
Instant puddings	X		X	X	X
Convenience desserts	X		X	X	X
Pie and cake fillings		X			X
Confectionery items		X			
Soup mixes	X		X		X
Batters, pancake, breading	X		X		
Toppings		X		X	
Ground meat & fish prod.		X			
Instant sauces and gravies			X	X	X
Dressings (salad type)	X			X	
Milk bev. stabilizers	X	X			

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Juice	Min.	Max.
Apple	0.2	3.6
Grape	0	4.7
Grapefruit	10.0	49.0
Orange	9.7	70.0
Pineapple	5.4	18.0
Tomato	2.5	32.0

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nology and research, made necessary by the fast-growing convenience food field. By proper evaluation and intelligent selection, the food processor can take advantage of their properties in a wide variety of food products, and benefit from the economies and improvements in food quality that they offer.

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Pink Discoloration in Canned Bartlett Pears

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In a previous publication *(11)*, the effects of cold storage and ripening on chemical and physical properties of Bartlett pears were investigated. It was observed that fresh Bartlett pears with average pressure tests of 2 to 3 pounds immediately before peeling were best for canning.

Pink discoloration in canned pears is an occasional problem to the canner. Such pears are undesirable because they fail to meet the U. S. Department of Agriculture color grade, and the unusual color causes concern to the canner and the consumer. The reason for this discoloration is not clear.

The biochemistry of apples and pears has been reviewed *(8)*, but no information about pink discoloration of canned pears has been mentioned. The presence of flavonoid compounds in the plants as glycosides, in which certain of the phenolic hydroxyl groups are combined with sugar residues, has been reviewed *(3, 4)*. Bate-Smith reported on anthocyanins and flavones *(1)*, leucoanthocyanins in leaves *(2)*, and flavonoid compounds *(3)* in foods. He also stated *(3)* that "leucoanthocyanins are themselves colorless, but give rise to red-brown colored products when heated in aqueous solution, especially if the solution is strongly acid. The color of stewed pears may well be due to leucoanthocyanins present in the fresh tissues, but this has apparently never been investigated." Sondheimer and Kertesz *(15, 16)* reported that the red pigment in strawberries was an anthocyanin. Griffiths studied the phenolic acids and flavonoids in cacao *(5)*. Hillis and Swain studied the influence of illumination on the synthesis of leucoanthocyanins in leaves *(7)*. Kieser, Pollard, and Williams *(10)* reported the presence of leucoanthocyanins in Perry pears, but presented no information on Bartlett pears.

In the present investigation the effects of growing area, soil types, and processing conditions on pink color development in canned Bartlett pears are reported. A method for quantitatively determining the pink-color precursor is presented. The pink pigment in the canned product was investigated by chromatographic methods.

EXPERIMENTAL MATERIALS AND METHODS

Bartlett pears. Pears used in this investigation were harvested from the Santa Clara, Lake County and Placerville areas at 16–19 pounds pressure tests on the Magness-Taylor fruit tester (5/16 in. plunger). Each lot contained about 200 pounds of fruit. The fruit was stored at 34° F. for 7 days or more, and ripened 4 to 5 days at 68° F. under 85% relative humidity until an average pressure test of two pounds was reached.

Physical and chemical tests. Ten representative pears were taken from each batch for determining pressure test, titratable acidity, pH, Brix, and tannin-like substances as described previously *(11)*.

Objective test for the pink-color precursor. Canned pears were mixed with the syrup in a Waring blender for 30 seconds. Ten grams of the sample was weighed into a 150 ml. beaker and 1.5 g. of sodium chloride, 2 ml. of 6N HCl, and 50 ml. of n-butanol were added. The mixture was stirred with a mechanical device for 15 minutes and then centrifuged to remove the insoluble solids. The supernatant was poured into a test tube, heated in a boiling water bath for 15 minutes (counting the time when the water started to boil) and cooled to room temperature in a water bath. The absorbance of the n-butanol extract was measured in a Klett-Summerson photoelectric colorimeter with a No. 42 blue filter.

Canning. Pears were peeled, halved, cored, and canned in No. 2½ cans. Eighteen ounces of pear halves and 11 ounces of 25° Brix sucrose syrup were used for each can. Unless otherwise stated, the pears were cooked in a stationary cooker at 212° F. for 33 minutes. The cans were either cooled in air or in cold water for different time intervals.

Heat increment. The temperature at the center of the can was recorded by a Brown Electronic Automatic recorder at 1 minute time intervals. The heat increment was obtained by counting the area under the temperature-time curve as recorded by the Brown recorder. Results were expressed as degree-minutes above 100° F. (37.8° C.).

Visual evaluation of pink color. The degree of pinkness in the canned pears was evaluated visually by a panel of 6 persons

under a standard light source *(11)*. Results were expressed as no pink (0), slight pink (+), medium pink (++), and very pink (+++).

Paper chromatography of the pink pigment. The pears and syrup from a No. 2½ can were mixed in a Waring blender. Forty-five grams of the slurry was mixed with 6.75 g. of NaCl, 6 ml. of 6N HCl, and 150 ml. of n-butanol. The mixture was stirred well for 15 minutes and then centrifuged. The supernatant was decanted into a beaker, heated for 15 minutes in a boiling water bath to develop the pink color and then concentrated under 27 in. of vacuum to a small volume. The concentrated extract was chromatographed at 70° F. for 12 hours on a Whatman No. 1 filter paper (in a descending direction) with the top layer of a n-butanol, acetic acid, water (4:1:5 v/v) mixture as solvent. The pink pigment was eluted from the paper with a mixture of methanol and concentrated HCl (97:3 v/v). The eluate was concentrated and purified once more on the paper. The pigment was dissolved in a 10% HCl solution, extracted with a few drops of n-amyl alcohol, and then chromatographed on Whatman No. 1 paper with n-butanol and 2N HCl (1:1 v/v). Cyanidin isolated from deep red roses by the method described by Yeh, Ling, and Takasaka *(17)* was used as a reference compound in the paper chromatography procedure.

RESULTS

Effect of growing area on pear composition. The composition of pears grown in 3 different areas of California is shown in Table 1. Sample 1 was from the Santa Clara area, and was

TABLE 1

Acidity, pH, and soluble solids content of Bartlett pears grown in different areas of California

Sample	Growing area	Titratable acidity, %	pH	Brix at 20° C.	Pressure test at canning, lbs.
1	Santa Clara	0.154	4.2	11.5	2.0
2	Sacramento River	0.287	4.0	12.1	2.0
3	Lake County	0.187	4.1	14.0	2.1
4	Lake County	0.506	3.9	14.0	1.7
5	Placerville	0.551	3.8	14.6	3.0
6	Placerville	0.503	3.8	13.7	2.5
7	Placerville	0.683	3.5	15.1	3.0

lowest in acidity and soluble solids, and highest in pH. Samples 3 and 4 were both from the Lake County area but differed greatly in their acidity and pH. It is evident that even in the same growing area, pear composition may differ greatly. This difference was probably due to variations in horticultural practices and soil properties of the ranches where the pears were grown. Samples 5, 6, and 7 were from the Placerville area located in the foothills of the Sierra-Nevada range. These pears were high in acidity and low in pH, probably due to climatic conditions or soil acidity of the ranches in the foothill area. The difference in acidity and pH of the pears from different growing areas was not caused by maturity, because they were all harvested and ripened to the same pressure range of 2 to 3 pounds, as measured by the Magness-Taylor pressure tester.

Influence of soil types on pear composition. The effect of soil types on acidity and pH of Bartlett pears is shown in Table 2. The acidity of the pear samples grown in Aiken loam, Diamond Spring loam, and Holland Sandy loam ranged from 0.30–0.45%, and the pH from 3.5 to 4.0. Thus, the nature of the soil could be another factor influencing pear acidity and pH.

Tannin content. The tannin content of samples shown in Table 2 varied from 92.5 to 152.8 mg./100 g. This seemed to be related to the pink discoloration of the canned product. Sample G was grown in a Holland fine sandy soil, had a tannin content of 152.8 mg./100 g., and was quite pink after canning. It seems that low pH, high titratable acidity, and high tannin content are all associated with pink discoloration in canned pears.

None of the samples canned by rapid water-cooling showed pink discoloration except Sample G, which was high in acidity and tannin and low in pH. Almost all of the Placerville pears canned by the air-cooling method (slow cooling rate) were pink. However, Sample I, which was low in tannin (92.5 mg./100 g.) and relatively high in pH (3.90) had no pink discoloration, even though the air-cooling method was used. Thus it seems that pink discoloration in canned Bartlett pears is also related to rate of cooling as well as high acidity, high tannin content, and low pH.

Objective test for the pink-color precursor. An objective test for determining pink color precursor in pears is described in the Experimental section. An example of pink color development in the acidified n-butanol extract is shown in Figure 1. Samples A and B developed a pink color similar to that in the canned product. However, if the heating was extended over 20 minutes, a brownish color gradually developed in the extract. The increase in absorbance caused by heating was shown to proceed in two stages. First, there was a rapid increase in absorbance with heating time, during which a characteristic pink color developed. Then there was a break after 20 minutes of heating. The rate of increase in absorbance with time slowed down and a brown color developed. Table 2 indicates that the Klett reading of the n-butanol extract might be a good indication of the pears' potential for pink color formation. Sample G was highest in the Klett butanol-extract reading and was pinkest after canning.

Effect of processing time and cooling rate. The effect of processing time and cooling rate on pink color development in canned pears is shown in Table 3. Pears from ranches M, I, and G showed no pink color formation when heat processed 25 or 30 minutes and rapidly cooled by water. However, in the sample from Ranch I, 17% of the pears developed pink discoloration after heat processing for 35 minutes at 212° F. This

TABLE 2

Influence of soil types on the chemical composition and pink discoloration of Bartlett pears. Placerville, California

Sample	Soil type	Fresh					Canned							
		Pressure test, 5/16 in. plunger	pH	Brix 20° C.	Titratable acidity, %	Tannin, mg./100 g.	pH		Titratable acidity, %		Klett reading in butanol extract (blue filter)		Degree of pinkness[1]	
							Water-cooled	Air-cooled	Water-cooled	Air-cooled	Water-cooled	Air-cooled	Water-cooled	Air-cooled
A	Aiken	3.39	3.75	14.94	0.411	125.0	4.00	3.85	0.260	0.278	83	89	0	+
B	Aiken	2.92	4.00	15.33	0.374	108.5	4.30	3.90	0.198	0.264	50	71	0	+
C	Aiken	2.80	3.85	14.93	0.457	116.2	4.20	3.85	0.247	0.303	54	70	0	+
D	Aiken	1.17	3.90	13.84	0.388	92.5	4.06	4.10	0.232	0.233	85	62	0	+
E	Diamond spring	2.90	3.85	14.74	0.371	128.5	4.10	4.20	0.216	0.214	80	59	0	+
F	Diamond spring	2.69	3.95	14.94	0.300	103.0	4.13	4.23	0.159	0.198	82	53	0	+
G	Holland fine sandy	2.20	3.50	15.54	0.363	152.8	3.76	3.60	0.216	0.220	112	100	+	++
H	Holland fine sandy	1.26	3.80	13.84	0.388	110.0	4.10	4.10	0.197	0.201	83	55	0	+
I	Holland fine sandy	2.72	3.90	15.44	0.370	92.5	4.10	4.00	0.224	0.237	68	27	0	0

[1] Degree of pinkness: 0 No pink; + Slight pink; ++ Medium pink; +++ Very pink.

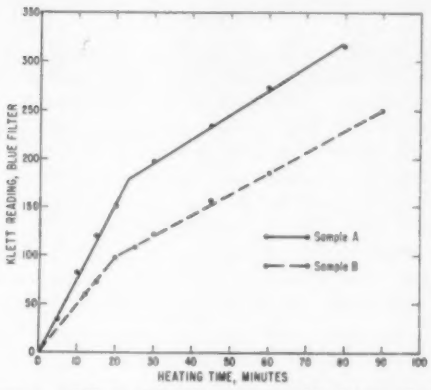

Figure 1. Effect of heating on the absorbance of acidified n-butanol pear extracts.

indicates the importance of processing time as well as raw material selection for preventing pink color formation in pears. Most of the canned pears that were air-cooled after canning were pink due to excessive heat.

Effect of acidification and delayed cooling. In order to prove that pink color formation and high acidity are related, an experiment was designed to determine the effect of acidification

TABLE 3

Effect of processing time and cooling rate on formation of pink color in canned Bartlett pears

Ranch	Soil type	pH of canned pears	Per cent pink pears					
			Rapid cooling in water, minutes of heating at 212° F.			Slow cooling in air, minutes of heating at 212° F.		
			25	30	35	25	30	35
M	Diamond spring loam	3.9–4.0	0	0	0	44	100	100
I	Aiken	3.6–3.7	0	0	17	63	90	78
G	Holland fine sandy loam	3.9–4.0	0	0	0	0	0	10

on pink color formation. Results are shown in Table 4. Sample 1, canned in syrup acidified to pH 1.4 with HCl, showed a deep pink color formation. Samples 2 and 5 were not as highly acidified and showed pink color only after air-cooling.

The effect of delayed cooling on pink discoloration of canned Bartlett pears is shown in Table 5. The water-cooled sample did not show any pink color formation, because the rapid cooling rate prevented it. The air-cooled samples showed a continual increase in pink color formation as accumulative heat increment rose from 4666 to 20884 degree-minutes above 100° F. These data indicate the importance of rapid-cooling in preventing pink color formation.

Nature of the pink pigment. The pink pigment, formed by heating the n-butanol extract of Placerville pears in the presence of HCl for 15 minutes, was purified by descending paper chromatography on Whatman No. 1 filter paper, using an n-butanol: 2N HCl (1:1 v/v) mixture as a solvent. The pigment had an R_f value of 0.68. This was identical to that of the cyanidin pigment isolated from roses. A mixture of the pink pigment from pears and cyanidin from roses resulted in only one spot on the paper. It seems that the pink pigment in canned pears is very similar or even identical to cyanidin which has the following structural formula:

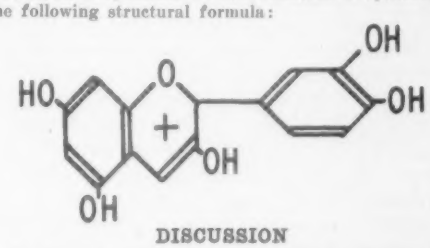

TABLE 4

Effect of acidification and cooling rate on formation of pink color in canned Bartlett pears

Lake County pears, cooked at 212° F. for 33 minutes					
Sample	pH of ingoing syrup	pH of canned pears	Per cent pink halves (water cooling)	Per cent pink halves (air cooling)	Degree of pinkness
1	1.4	3.3	38	100	+++
2	2.1	3.4	0	50	+
3	2.3	3.5	0	100	+++
4	5.8	3.5	0	56	+
5	6.0	3.7	0	29	+

TABLE 5

Effect of delayed cooling on pink discoloration of canned Bartlett pears from Placerville, California

Time after heating at 212° F. for 33 min.	Air-cooled			
	Heat increment above 100° F., °F. x min.	Accumulative heat increment above 100° F., °F. x min.[1]	% total heat received	Degree of pinkness
(min.)				
0	3696	4666	22.3	0
2	214	4880	23.3	+
5	309	5189	24.8	+
10	500	5689	27.2	+
20	970	6659	32.1	+
25	470	7129	34.1	++
45	1740	8869	42.5	++
60	1155	10024	48.0	++
90	2010	12034	57.6	++
120	1620	13654	65.4	+++
180	2280	15934	76.3	+++
300	4950	20884	100.0	+++

[1] This reading includes the heat received during water-cooling of the pears from 212° F. to 100° F.

DISCUSSION

It has been shown that pears from different growing areas vary greatly in acidity, pH, and tannin-like substances. Such differences in the fresh pears are related to the formation of pink color in the canned product. One way to prevent pink color formation is to check fresh pears for these properties prior to canning. Pears with exceedingly low pH, high tannin content or high absorbance in the acidified n-butanol extract should be sent to a packing house for fresh marketing. The majority of the pears in California have pH values ranging from 3.9 to 4.2. It would be possible to screen out those pears with low pH that are likely to form pink color after canning. A second approach is to check the canning operation closely. Excessive heat sterilization must be avoided. Prompt water cooling of the cans after heat sterilization would help reduce the occurrence of pink color in the canned product.

Results obtained in this work indicated that pink color formation in canned pears from certain districts could be greatly increased by lowering the pH values with hydrochloric acid. This indicates that the formation of pink color is catalyzed by the hydronium (H_3O) + ion. The same reaction is facilitated by excessive heating which supplies the activation energy necessary for pink color formation.

In the 1938 U. S. Department of Agriculture year book, *Soil and Men*, it is stated that the lower Sierra-

Nevada foot hills have an elevation of 300-5000 feet. The area has a long dry summer with a high percentage of sunshine, and weak to mild acid in the Sierra and Holland soils. Thus it is highly possible that the higher incidence of pink color in canned Bartlett pears from some of the ranches in the Sierra foot hill area might be caused by soil property and climatic conditions.

The presence of leucoanthocyanins in Perry pears has been reported by Kesser, Pollard, and Williams *(10)*. After chemical and chromatographic tests, they suggested that the major component of pear tannin is a complex leucoanthocyanin of high molecular weight, composed of units similar in structure and hydroxylation pattern to cyanidin. Results obtained in the present investigation also indicate that the pink pigment is not differentiable from cyanidin by paper chromatographic method. Joslyn and Peterson *(9)* reported the presence of leucoanthocyanin in the core, tissue, and seeds of Bartlett pears. They concluded that the only anthocyanidin obtained was similar in R_f value and other properties to cyanidin.

Although cyanidin formation seemed to accompany pink discoloration of canned Bartlett pears, it is still possible for pigments other than anthocyanin to be present. Recently, Lukes *(12)* reported on the formation of pink pigment in dehydrated onions. He postulated that when the onion cells are ruptured, the native enzymes react with a substance in the juice to form a color developer. This developer then non-enzymatically forms a pink pigment with the amino-acids in the onions. Peterson *(13)* postulated that the pink pigment in dehydrated onions was due to a water-soluble, nitrogenous cation fraction, formed from unknown precursors during the period immediately after macerating. This cation fraction reacts non-enzymatically with added formaldehyde or some naturally-occurring compound at pH 2 to 6 to form a water-soluble, red pigment. In canned pears the pink pigment usually adhered to the surface of the pear. However, in severe cases, when the pink pigment was present in high concentrations, the syrup also turned pink.

It remains to be explained why only some of the pear halves turn pink after canning. This might be due to the localization of pink-color precursor in certain parts of the pear fruit. Hillis and Swain *(7)* studied the effect of illumination on the leucoanthocyanin content of plum tree leaves. They found a lower leucoanthocyanin and total phenol content in leaves on the shady side of the tree, than in those on the sunny side. It is possible that parts of pears exposed to the sun may develop higher leucoanthocyanin contents than other parts. This might explain the pink color formation in only part of the pears after canning.

SUMMARY

Factors influencing formation of pink color in canned Bartlett pears have been investigated. Growing area and soil types were found to be related to this problem. Pears from certain growing areas had low pH, high acidity, and high [illegible]a content. These pears were found to develop pink color after canning, especially when excessive heating and delayed cooling processes were used. The pink pigment in canned pears was shown to be identical in R_f value to that of cyanidin. An objective test for determining the amount of pink color precursor in pears is described.

Acknowledgment

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Characteristics of Corn Starch and Starch Derivatives as Affected by Freezing, Storage and Thawing. I.

Simple Systems[a]

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UNDESIRABLE TEXTURE CHANGES are frequently encountered in the freezing of cooked foods thickened with common starches. The texture of sauces, gravies, puddings, and custard-type desserts changes from a smooth to a grainy or lumpy consistency even when these foods are thawed immediately after freezing. When thawed after some time in frozen storage, most such products exhibit a curdled appearance and liquid separation. The original smoothness is not completely regained even in foods that are reheated before serving *(4, 5, 10)*. Such texture changes as those described above have been commonly grouped under the term "retrogradation" *(6, 9)*.

Freezing of a starch solution causes the starch to separate and to remain, after thawing, as a fibrous and flocculent coagulum. When 2.5% corn starch pastes are frozen, thawed and warmed to 212° F., about 93% of the starch remains insoluble *(3)*. Corn and wheat starch pastes of 5% or higher concentration become a spongy mass upon freezing and thawing *(8, 12)*. Slow freezing of the solution is said to produce larger aggregates of coagulum than does rapid freezing *(7)*. In addition, the condition of a thawed gel depends upon the temperature to which it has been cooled; spongy gels thawed from solutions frozen at −94° F. are more slimy than gels from solutions frozen at 28° F.

A system that exhibits "freeze-thaw stability" is one that does not become lumpy, grainy or spongy, is free from liquid separation (syneresis), and remains homogeneous after it has been frozen, stored at low temperatures, and finally thawed to room temperature.

The effects of various physical treatments on the stability of frozen starch pastes have been studied by various workers. Included in this category are a series of investigations relating to different granule shearing treatments *(2, 11)*. However, the conclusions reached in these studies have been inconsistent.

The over-all objective of this investigation was to determine the effects of rate of freezing, storage temperature, shearing of granule systems, and heat treatment prior to freezing on the freeze-thaw stability of the simple combination of thickening agent and water. Three starch products were chosen to serve as a representative group of thickening agents: (1) a standard or natural corn starch, (2) a pregelatinized cross-linked waxy maize starch, and (3) a starch phosphate.

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EXPERIMENTAL PROCEDURE

Ingredients

The starch considered to be of most importance in this investigation was regular untreated corn starch (Reg. PFP, American Maize Products Co., Roby, Indiana), because this starch has been used as a food thickener for many years. The second product studied was HR W-13—a pregelatinized, cross-linked waxy maize starch (American Maize Products Co.). Solutions of this starch, after heating and cooling, offered increased viscosity but did not set up in a typical starch gel. To represent one of the latest types of starch-derivative thickening agents being studied a starch phosphate sample (International Minerals and Chemical Corp., Skokie, Illinois) was used. This product is soluble in cold water, produces a paste of unusual clarity and homogeneity, and has essentially no starch taste.

Analytical procedures

The susceptibility of starch pastes and slurries to the action of a commercial β-amylase preparation is called "amyloclastic susceptibility." Less retrogradation allows increased hydrolytic activity of this enzyme to form more maltose. Enzyme susceptibility was determined by the method of Volz and Ramstad *(11)*, although a few modifications in sample size were necessary, as described by Albrecht *(1)*.

Since starch systems which have undergone retrogradation generally are unable to bind water tightly, measurement of syneresis or "weeping" usually can be correlated with the degree of retrogradation which has taken place. To measure syneresis, aluminum weighing dishes two inches in diameter and ⅞ inches deep were filled with starch paste and allowed to remain at room temperature for 2 hours. Dishes were then inverted on No. 3 filter paper and the annular ring of wet paper was measured in sixteenths of an inch after exactly two minutes.

Photomicrographs of certain samples of starch pastes were taken by a Zeiss Inclined Triocular Microscope, Model GF 595, equipped with a Micro-Ibso attachment and Kodak film-holder. In order to obtain photomicrographs of samples of starch phosphate, it was necessary to use a negative staining technique in which the slide was flooded with India ink by placing a drop of the ink next to the cover glass.

Processing procedures

Preparation of Starch-Water Slurries: Two different techniques were used to prepare starch-water slurries for this study. The first such procedure was designed to produce a product in which the starch had not been gelatinized and in which the granules were, for the most part, undamaged and unswollen. In this procedure, starch and water were added to the steam jacketed bowl of the 30 qt. Hobart mixer, Model S 301, operating on No. 1 speed. The mixer was then set on

No. 2 speed for a total of 10 minutes. Steam at 4 p.s.i.g. was admitted to the jacket of the mixing bowl during the last 2 minutes of mixing; this resulted in a final product temperature of 145–150° F. This heating was not sufficient to cause gelatinization of the starch.

The second procedure was designed to yield a product which had been heated for sufficient time to insure maximum swelling and gelatinization of the granules. This heating and mixing procedure was similar to that described above except that a product temperature of 185–190° F. was reached.

Five per cent tapwater slurries of regular corn starch and of pregelatinized, cross-linked waxy maize starch and three per cent slurries of starch phosphate were prepared. The hot viscosity readings of the several starch slurries were similar. Product was filled into No. 1 enameled cans with one-quarter inch headspace. The cans were then sealed, divided into 2 equal lots, and immediately placed at 0° or −40° F. storage. Before freezing and after regular intervals, samples were removed from storage and determinations made for enzyme susceptibility and separation of free liquid.

Freezing and Thawing: To examine the effect of freezing and storage temperature on the freeze-thaw stability of starch slurries, 5% slurries of Reg. PFP and HR W-13 starches were prepared using the techniques described above. Samples were evaluated before freezing and after freezing and storage at temperatures of 20°, 10°, 0°, and −40° F. for 1, 7, 14 and 30 days.

Liquid nitrogen (−196° F.) was used to achieve virtually instantaneous freezing in another part of the study. Samples of starch slurry were filled into a 20 cc. Luer-Lok syringe equipped with a No. 14 needle. By applying slight pressure to the syringe plunger, uniform droplets of approximately ⅛ inch diameter were made to fall directly into liquid nitrogen. A set of samples of the starches was instantaneously frozen as described above and stored at 0° F. for 1 week and 1 month.

Unless otherwise indicated, samples were thawed in the original cans in a water bath at 100 ± 5° F. This process required from 1 to 2 hours. In one experiment a Radarange unit (an electronic oven produced by Hotpoint Co., Chicago, Ill.) was used to achieve thawing in less than 10 minutes.

Shearing of Starch Slurries Prior to Freezing: Various shearing treatments were carried out with a colloid mill, a homogenizer, and a comminuting machine. Two different amounts of shearing were effected in a type L.P. laboratory colloid mill (Manton-Gaulin Mfg. Co., Everett, Mass.). With the mill set for a clearance of 0.005 inches between discs, starch slurries were passed through the mill either one time or recirculated for a total period of 5 minutes which allowed about seven passes through the machine. A similar pair of treatments was made with a 2-stage piston type homogenizer (Manton-Gaulin Mfg. Co., Everett, Mass.). The first treatment involved passing the starch slurry through the unit once using a pressure of 2500 p.s.i.g. In the second method one quart of starch slurry was recirculated for a total of 5 minutes or about seven times, with a pressure setting of 3500 p.s.i.g. When the Model D comminuting machine (W. J. Fitzpatrick Company, Chicago, Ill.) was used the slurry was passed through the mill a total of 4 times. The comminuting machine was run at 4420 r.p.m. and equipped with a 1/32 inch screen. A control, unsheared set of samples was prepared with each treatment.

High-Temperature Treatment of Starch Slurries: A laboratory end-over-end agitating retort *(1)* was used to heat starch slurries to relatively high temperatures (200°-300° F.). Number 1 cans were filled with a 185°–190° F. starch slurry using ¼ inch headspace and sealed immediately. One can was equipped with a thermocouple connected to a recording potentiometer in order to follow the temperature rise at the center of the can. The sealed cans were placed in the agitating retort and heated. After 8 minutes from steam-on to steam-off, the cans were pressure cooled to about 100° F., removed from the retort, and immediately placed in 0° F. storage.

Preparation of Slurries for Analysis after Thawing: Thawed samples were placed in a steam jacketed mixing bowl of a Kitchen Aid mixer. The mixer was operated without heating at No. 2 speed for 5 minutes after which enough sample was removed to carry out the various required tests. The material remaining in the bowl was allowed to mix, with heating, for an additional 10 minutes. These 2 samples were referred to as A (thawed, but not reheated) and B (thawed and reheated), respectively.

RESULTS AND DISCUSSION

Starch which has undergone retrogradation is not attacked by β-amylase. Workers *(11)* have made use of this fact in studying retrogradation of starch-water systems. Unless exceptional care and precautions are taken, measurements of viscosity, weeping or free-liquid separation, and similar physical properties do not yield the degree of accuracy and reproducibility obtained in measuring enzyme susceptibility.

Statements describing gross changes in appearance which occurred in starch slurries during freezing, storage, and thawing, were recorded. Comparison of data for Reg. PFP starch preheated at 185° F. in Table 1 indicates that enzyme susceptibility measurements are related to gross changes in physical appearance. Figure 1 depicts the appearance of Reg.

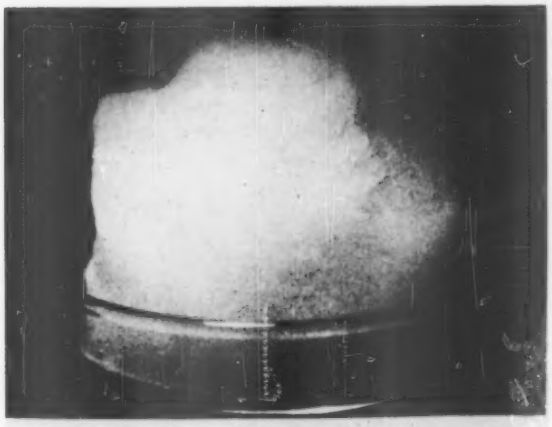
TABLE 1

Effect of freezing and storage conditions on enzyme susceptibility and gross physical appearance before freezing and after thawing

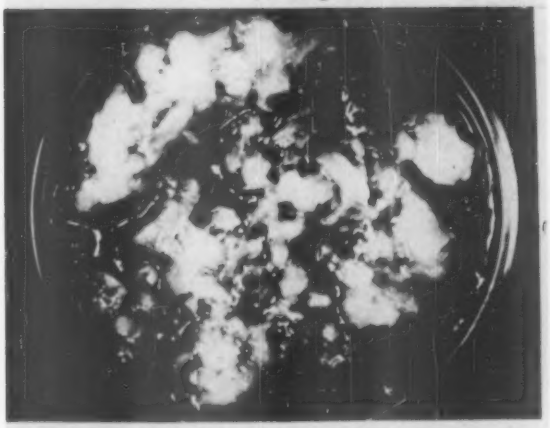
Starch and preheat temp.	Storage temp., °F.	Days storage			Gross physical appearance	
		0	1	30	Before freezing	After thawing, without mixing
		Enzyme susceptibility, E.S. units[1]				
Reg. PFP at 145° F.	20	5.5	5.7	5.3	Milky suspension	Coarse, milky suspension
Reg. PFP at 145° F.	10	5.5	5.6	5.7	Milky suspension	Coarse, milky suspension
Reg. PFP at 145° F.	0	5.5	5.3	5.1	Milky suspension	Coarse, milky suspension
Reg. PFP at 145° F.	−40	5.5	5.6	5.5	Milky suspension	Coarse, milky suspension
Reg. PFP at 185° F.	20	26.9	16.0	14.3	Smooth gel	Loose sponge; free liquid
Reg. PFP at 185° F.	10	26.9	16.5	13.0	Smooth gel	Loose sponge; free liquid
Reg. PFP at 185° F.	0	26.9	11.6	10.8	Smooth gel	Loose sponge; free liquid
Reg. PFP at 185° F.	−40	26.9	15.0	14.8	Smooth gel	Sponge—extremely loose
HR W-13 at 145° F.	20	28.0	25.7	25.6	Syrupy	Lumpy; coarse
HR W-13 at 145° F.	10	28.0	25.1	25.0	Syrupy	Lumpy; coarse
HR W-13 at 145° F.	0	28.0	22.0	24.0	Syrupy	Lumpy; coarse
HR W-13 at 145° F.	−40	28.0	26.3	27.0	Syrupy	Lumpy; coarse
HR W-13 at 185° F.	20	29.6	27.6	26.6	Syrupy	Heterogeneous; lumpy
HR W-13 at 185° F.	10	29.6	27.0	26.0	Syrupy	Heterogeneous; lumpy
HR W-13 at 185° F.	0	29.6	25.7	25.7	Syrupy	Heterogeneous; lumpy
HR W-13 at 185° F.	−40	29.6	29.0	29.0	Syrupy	Heterogeneous; lumpy

[1] Sampled after thawing and mixing for 5 minutes without heating (Post-thaw treatment A).

PFP starch pastes after thawing. In trying to explain the relationship between retrogradation resulting in sponge formation and amyloclastic susceptibility of regular corn starch, it may be theorized that a tight alignment of amylose molecules is caused by retrogradation. Thus, it becomes increasingly difficult for the enzyme to penetrate the micellar areas of the starch molecule.



After Thawing



After Thawing and Mixing 5 Minutes

After Thawing and Reheating 10 Minutes

Figure 1. Photographs of sponge development in Reg. PFP starch slurries after freezing and thawing.

Effects of preheating temperature

Using 5% slurries of Reg. PFP and HR W-13, and 3% slurries of starch phosphate (SPHV), portions were heated either to 185° F. or to only 145° F., as described previously.

In Figures 2, 3, and 4, data have been incorporated concerning both the gross physical appearance of the experimental samples and the corresponding enzyme susceptibilities of these same samples. There was a definite decrease in the enzyme susceptibility of 5% slurries of gelatinized (preheated to 185° F.) regular corn starch when such slurries were exposed to sub-freezing temperatures. These samples, which were smooth gels prior to freezing, exhibited sponge formation and syneresis after freezing and thawing.

It was shown that slurries of Reg. PFP are stable to freezing when the granules are not gelatinized (preheated to 145° F.) prior to freezing. By considering groups 3 and 4 in Figure 2, representing Reg. PFP slurries which had been heated above the gelatinization point, it is seen that this gelatinization resulted in undesirable sponge formation (solid, dark bars). Comparable slurries (Figure 2, Groups 1 and 2) which had not been pregelatinized were coarse milky suspensions after thawing (horizontal, shaded bars).

Various preheating treatments did not have an appreciable effect on the stability of frozen slurries of HR W-13 or starch phosphate (Figures 3 and 4). Enzyme susceptibility decreased more in samples stored at 0° F. than at −40° F. (Figure 3, Groups 2 and 4).

Figure 5 contains photomicrographs of starch phosphate samples before and after heat treatment at 145° F. and 185° F. These show that while the granules lose their sharp outlines, the basic size and shape of these granules remains essentially unchanged after heat treatment.

When sponges or other insoluble conglomerates were formed, it was found that reheating the thawed samples for 10 minutes greatly reduced the spongy or lumpy consistency and caused the enzyme susceptibility to rise to a level comparable with that of corresponding samples which did not exhibit any of these undesirable characteristics either before or after freezing (e.g., E.S. values of 29.1 and 30.2, respectively). However, the appearance of the reheated samples was noticeably grainy in most cases (Figure 1).

To illustrate the importance of the gelatinization point as related to freeze-thaw stability, a set of samples of Reg. PFP starch similar to those described above was prepared in such a way that the samples reached maximum temperatures of 155°, 163°, and 170° F. The samples were allowed to remain at

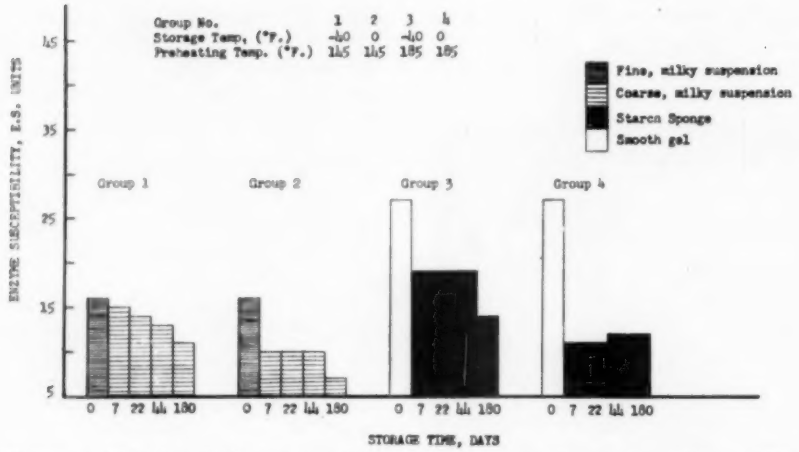


Figure 2. Effect of preheating, storage temperature and storage time on freeze-thaw stability of 5% slurries of regular corn starch.

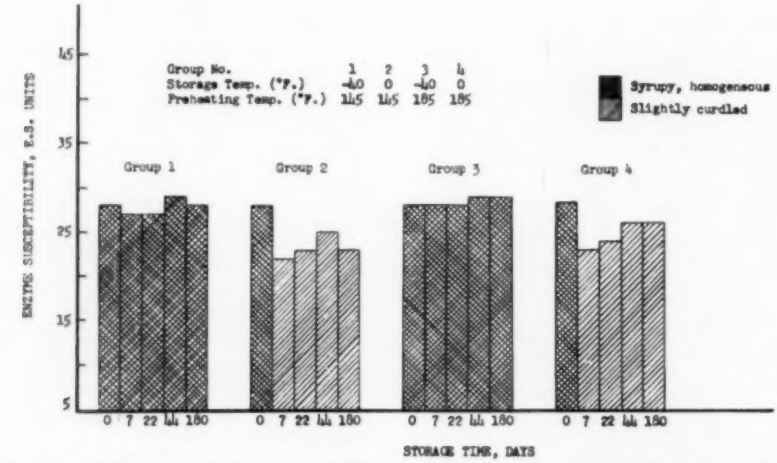


Figure 3. Effect of preheating, storage temperature and storage time on freeze-thaw stability of 5% slurries of HR W-13 waxy maize starch.

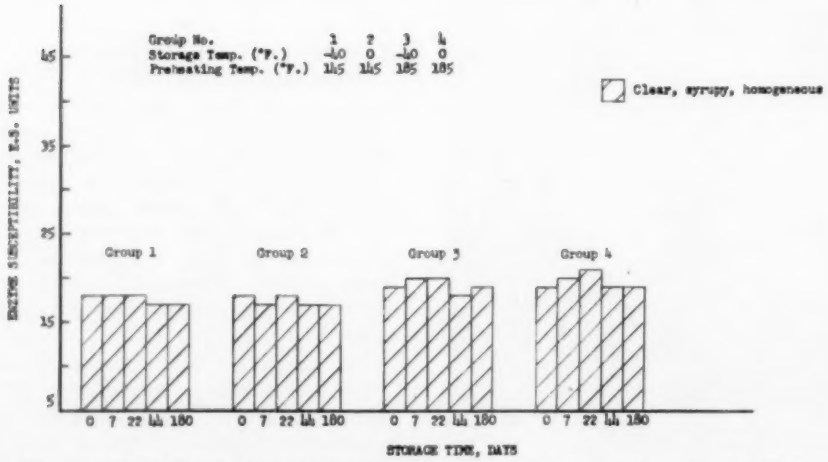
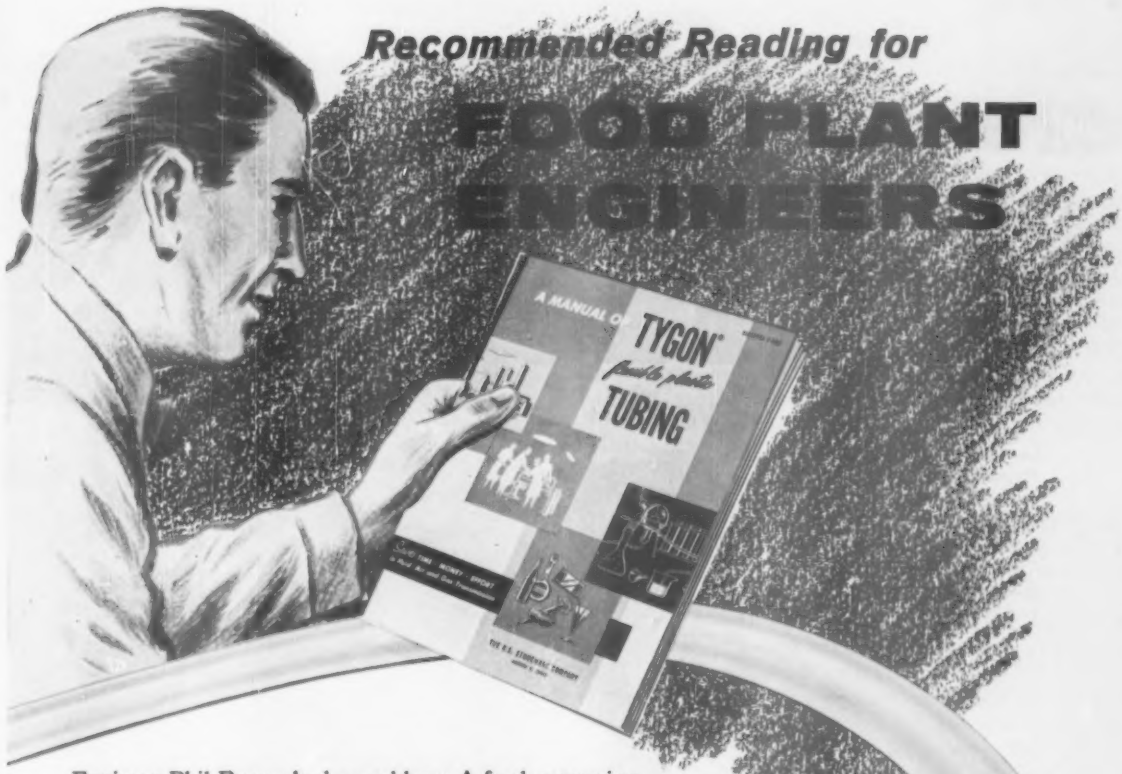


Figure 4. Effect of preheating, storage temperature and storage time on freeze-thaw stability of 3% slurries of starch phosphate.



Engineer Phil Brown had a problem: A food processing operation in his plant was being expanded, necessitating rearrangement of existing units and installation of new equipment. New pipelines had to be provided to convey liquid and semi-solid foodstuffs—and time was at a premium! Down time had to be held to an absolute minimum, so the changeover would have to be made fast. But conventional piping installations take time . . .

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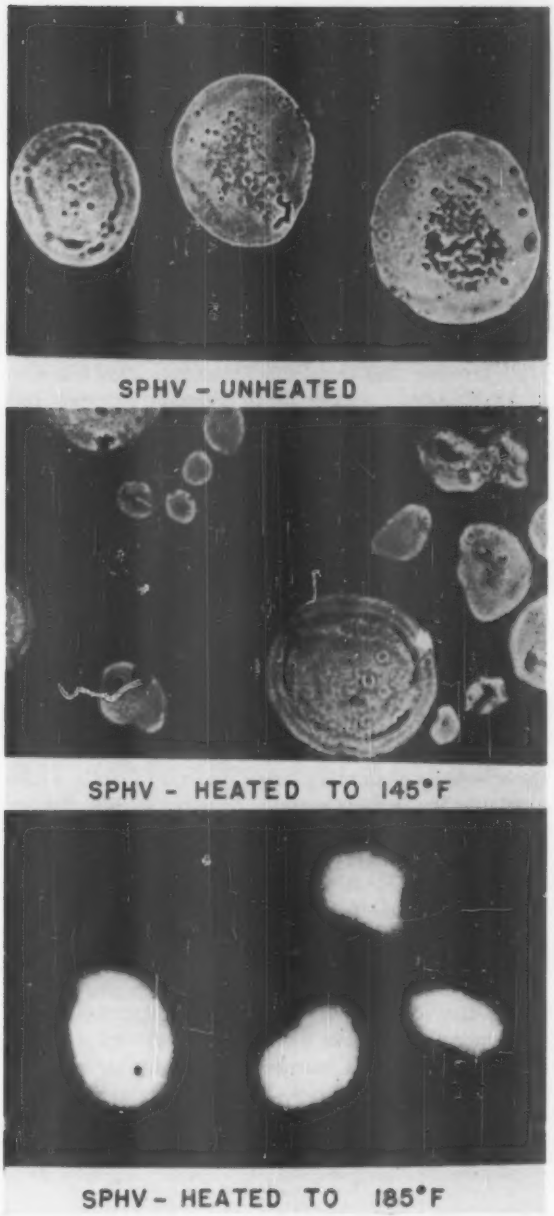

Figure 5. Photomicrographs of a starch phosphate slurry before treatment and after heating to 145° F. and 185° F.

these maximum temperatures for exactly ten minutes. Samples were then canned and stored at 0° F.

Table 2 contains data which indicate that once the starch slurry reached the critical gelatinization temperature of 163° F., the typical undesirable changes such as sponge formation and syneresis occurred in the frozen and thawed samples, thereby making the slurry undesirable for use in precooked frozen food products. There was essentially no difference between the sample heated to the critical gelatinization temperature and all samples which had been heated to as high as 185° F. The samples which had been heated to a maximum temperature of 155° F. exhibited none of the above undesirable properties (Table 2), and were similar in all respects to those preheated to 145° F.

Effect of freezing and storage temperature

The effects of freezing and storage temperature are presented in Table 1. The data for 7 and 14 days' storage were omitted because they were essentially the same as for the 30-day storage shown.

Although enzyme susceptibility data indicated that the rate of retrogradation was higher at a freezing and storage temperature of 0° F. than at −40° F., this fact was not readily observed in the gross physical appearance of the samples. Essentially no differences in appearance between comparable samples stored at various temperatures are found in Table 1. Since the enzyme susceptibility data show that considerable retrogradation occurred at 0° F., the temperature commonly recommended for storage of frozen foods, subsequent starch slurries were stored at this temperature.

Because the preceding studies indicated that the rate of retrogradation was noticeably lower at −40° F. as compared to 0° F., representative sets of samples of pregelatinized Reg. PFP and HR W-13 starches were prepared and frozen by direct immersion in liquid nitrogen. One set of samples was evaluated immediately after freezing; a second set was placed in 0° F. storage to observe whether changes in freeze-thaw stability would occur in frozen storage even after instantaneous freezing. Because extremely rapid freezing was used, it was considered desirable to compare rapid thawing in a Hotpoint Electronic Range with conventional slow thawing in a 100° F. water bath. Six minutes in the electronic unit brought the samples to room temperature, whereas 60 minutes were required to do this in the water bath. Results of these experiments are shown in Table 3.

TABLE 2

Freeze-thaw stability of 5% slurries of regular corn starch preheated to various temperatures and stored at 0° F.

Preheating temp., 0° F.	Days storage							
	0	1	7	17	0	1	7	17
	Enzyme susceptibility, E.S. units				Liquid separation, in sixteenth inch			
155	11.0	7.8	7.0	6.8	*	*	*	*
163	26.7	10.1	8.2	7.7	0	19	23	23
170	26.3	9.6	8.1	7.8	0	20	24	24

* Not gelatinized; a blotter test for liquid separation could not be used.

TABLE 3

Effect of instantaneous freezing and rapid thawing on freeze-thaw stability of Reg. PFP pregelatinized starch slurries

Treatment	Days storage at 0° F.			Days storage at 0° F.		
	0	1	7	0	1	7
	Enzyme susceptibility, E.S. units			Liquid separation in sixteenth inch		
Frozen in liq. N_2, thawed in electronic oven after storage	28.3	28.0	23.0	1	2	2
Frozen in liq. N_2, thawed in water bath after storage	27.9	28.1	28.4	3	3	3
Control (not frozen in liq. N_2). Thawed in water bath after storage	27.9	14.5	11.3	0	12	14

Instantaneous freezing eliminated sponge formation from samples of Reg. PFP starch and the curdled post-thaw appearance from HR W-13 samples. All samples frozen in liquid nitrogen retained their original properties, both immediately after freezing and after storage at 0° F. for one week. This latter observation is of particular importance since in almost all other storage studies it was observed that considerable retrogradation took place during the first few days storage at 0° F. A storage period of one week is not of sufficient length to justify any conclusive statements concerning the occurrence of retrogradation over storage periods of much longer duration. The data do, however, indicate that smaller ice crystals representing a more dense system decreased the likelihood of molecular alignment necessary for retrogradation.

Within the limitations of this study extremely rapid thawing in the electronic range did not appear to offer any major advantages over thawing in a water bath at 100° F. This does not agree with the findings of earlier workers *(7)*.

Effects of shearing treatments on freeze-thaw stability

Slurries of Reg. PFP and HR W-13 starches were prepared and subjected to the actions of 3 different types of shearing devices. Control, unsheared samples were also prepared for each treatment. Shearing of starch slurries by means of the colloid mill, the Fitz Mill, and the homogenizer did not appreciably affect the enzyme susceptibility of the samples. In the case of regular corn starch, all prepared samples cooled to smooth gels immediately after shearing treatment. Sheared slurries which were then frozen and later thawed all exhibited sponge formation, regardless of type of shearing treatment. Similarly, waxy maize samples were smooth and homogeneous before freezing, but were curdled and lumpy after freezing and thawing. There was some question as to whether any significant granule shearing had actually taken place. To clarify this point, photomicrographs were taken and it was noted that essentially no granule damage had been effected.

The effect of more severe shearing treatment was studied with Reg. PFP and HR W-13 starch slurries. Photomicrographs showed that homogenizing a HR W-13 sample at 3500 p.s.i.g. resulted in severe shearing in contrast to the lack of shearing at 2500 p.s.i.g. as described above. A comparison was made between these moderate and severe shearing treatments as they affect the enzyme susceptibility of starch slurries. Table 4 summarizes this comparison. This extreme reduction of granule size did not result in a major increase in enzyme susceptibility even though there was a considerably larger amount of surface area available for enzyme attack. Apparently, the enzyme susceptibility of a starch in suspension is not a function of particle size, but is probably directly related to porosity of the starch granule.

Effects of treatment at high temperature

In order to determine the effect of high temperature, slurries were prepared by preheating to 185° F., filling into Number 1 cans and rapidly heating to high temperatures in an end-over-end agitating retort. Samples of 3 starches were heated simultane-

TABLE 4

Comparison of moderate with severe shearing on enzyme susceptibility of starch slurries frozen and stored at 0° F.

Starch	Preheating temp., °F.	Type of shearing action	Days storage			
			0	1	7	15
			Enzyme susceptibility, E.S. units			
Reg. PFP	145	Control	5.5	5.3	5.9	7.9
Reg. PFP	145	Homogenized—2500 p.s.i.g.	5.0	4.8	5.3	5.7
Reg. PFP	145	Homogenized—3500 p.s.i.g. for 5 minutes	5.2	5.0	6.0	6.3
Reg. PFP	185	Control	26.9	13.7	14.0	14.8
Reg. PFP	185	Homogenized—2500 p.s.i.g.	26.6	16.1	16.3	16.1
Reg. PFP	185	Homogenized—3500 p.s.i.g. for 5 minutes	28.6	19.0	17.3	17.7
HR W-13	145	Control	27.2	23.8	22.6	22.8
HR W-13	145	Homogenized—2500 p.s.i.g.	27.0	24.1	23.0	22.6
HR W-13	145	Homogenized—3500 p.s.i.g. for 5 minutes	25.5	20.9	20.7	20.8
HR W-13	185	Control	29.7	26.8	25.7	26.0
HR W-13	185	Homogenized—2500 p.s.i.g.	29.3	27.4	27.3	27.0
HR W-13	185	Homogenized—3500 p.s.i.g. for 5 minutes	30.1	29.2	29.0	28.8

ously at the experimental temperature to minimize error. From the data in Table 5 it seems evident that the rate of starch retrogradation at 0° F., as measured by enzyme susceptibility, appears to be a function of the degree of heat treatment received prior to freezing. Starch slurries which were treated at very high temperatures appeared to retrograde at a slower rate. However, as shown in Table 5, even samples processed at 300° F. were far from acceptable in gross physical appearance after freezing and thawing.

TABLE 5

Effect of high-temperature processing on enzyme susceptibility and physical appearance of Reg. PFP starch slurries frozen and stored at 0° F.*

Preheating temp., °F.	Days storage			Gross physical appearance	
	0	1	60	Before freezing	After thawing
	Enzyme susceptibility, E.S. units				
225	27.0	10.9	10.9	Smooth gel	Sponge
250	27.5	11.3	15.0	Smooth gel	Tough sponge
270	27.2	13.1	14.0	Slippery	Tough sponge
300	27.5	19.1	14.0	Slippery	Sponge

*All of the samples in this particular study were thawed and mixed for five minutes without heating in the Kitchen Aid mixer prior to sampling for various tests (Post-Thaw Treatment A).

SUMMARY

Effects of various processing variables on the freeze-thaw stability of starch slurries were investigated. Two starches and a starch derivative were included. Other variables were processing of the slurry, rate of freezing, storage temperature, thawing and post-thaw treatment. The susceptibility of the starch to enzyme action generally decreased with an increase in starch retrogradation as indicated by sponge formation, syneresis, and lumpiness.

Retrogradation was essentially eliminated from frozen Reg. PFP starch slurries which had not been heated to the critical gelatinization temperature.

It was shown that the enzyme susceptibility of slurries of HR W-13 starch and starch phosphate did not significantly change as a result of freezing and thawing. Similarly, preheating of such slurries to temperatures as high as 185° F. had no noticeable effect on freeze-thaw stability.

Retrogradation was found to take place at the most rapid rate during the 24-hour period after the starch slurries had been placed in frozen storage, and continued to take place at a much slower rate during subsequent storage.

Freezing starch slurries instantaneously by direct immersion in liquid nitrogen made it possible to eliminate sponge formation from samples of pregelatinized regular corn starch and the curdled appearance from waxy maize slurries. After storage at 0° F. for one week, samples frozen by this method gave no indication of retrogradation.

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Characteristics of Corn Starch and Starch Derivatives as Affected by Freezing, Storage and Thawing. II.

White Sauces[a]

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In recent years, the increased interest in precooked frozen foods for the retail market has encouraged development of such items as frozen meat pies, frozen tray dinners, frozen stews, and other gravy-containing mixtures. The stability of white sauces or gravies which can be used in such precooked frozen foods has been studied *(2, 4, 5, 6)*. Some workers have attacked this problem with regard to the effect of specific additives such as sugars, acids, fats, and proteins on the stability of starch-thickened sauces *(12)*. Others have been interested in the effect of the same additives in simple starch-water systems *(10, 11)*. A lesser amount of work has been done on the effect of physical treatments on frozen white sauce stability.

Hanson *(4)* points out that separation of free liquid or "weeping" and the curdling that develops due to starch retrogradation when such sauces or gravies are frozen are generally regarded *(3, 8)* to be important quality defects. This unsightly appearance reduces consumer acceptance.

Food processors are in need of a thickening agent which would be stable to freezing and frozen storage. Hanson *(4)* has suggested that salad dressings and desserts (puddings, custards, etc.) as well as sauces and gravies could be prepared as stable and very acceptable precooked frozen foods providing the right thickening agent or combination of thickening ingredients could be found. More recent applications include frozen pies, frozen baby foods, and frozen condensed soups. The increased demand for precooked frozen foods warrants further investigation of the factors involved in the low temperature stability of thickening agents.

Prior to this study, an investigation was carried out on basic starch-water systems *(1a)*. Three radically different thickening agents were investigated to determine the effects of preheating treatments, freezing and storage temperatures, starch granule shearing by physical means, and high temperature treatment on the freeze-thaw stability of starch-water systems. Many of the techniques and results from these earlier studies were utilized in this investigation.

The objective of this research was to produce a typical white sauce system stable to freezing, frozen storage and subsequent thawing at room temperature. Of special significance in the present study was the use of high-pressure homogenization techniques and instantaneous freezing of white sauce systems using liquid nitrogen. Other treatments involved gelatinization and storage temperature effects. Replicated samples were organoleptically evaluated.

EXPERIMENTAL METHODS

Sauce ingredients. Three starches were included in this investigation, namely regular corn starch (Reg. PFP [d]), pregelatinized, cross-linked waxy maize starch (HR W-13 [d]), and starch phosphate (SPHV [e]). The only other thickening agent was a commercial all-purpose flour. Skim milk (0.5% butterfat or less) was obtained from a local dairy. The fat was Crisco, a hydrogenated vegetable oil shortening. Ordinary table salt was the remaining white sauce ingredient.

Equipment. The Model S 301 Hobart mixer described in the previous paper *(1a)* was equipped with a whip attachment for preparation of white sauces. The two-stage Manton-Gaulin Type 25 CGB homogenizer was employed to shear white sauces at a pressure of 3500 p.s.i.g. and a rate of 22 cc. per second.

Analytical procedures. The test for amyloclastic susceptibility described by Volz and Ramstad *(9)* as modified by Albrecht *(1)* was used. Syneresis was determined by the standard blotter test. Since starch systems which have undergone retrogradation generally are unable to bind water tightly, measurement of syneresis or weeping usually can be correlated with the degree of retrogradation which has taken place.

Preparation of white sauces. Standard white sauces were prepared from each of the 4 thickening agents previously described. Ingredients used in the sauces were each obtained from a single source to minimize variations in results due to ingredient variations. The amounts of fat, salt, and skim milk remained constant per batch for all thickening agents: fat—400 g., salt—57.6 g., and skim milk—8656 g.

The amount of thickening agent used in each case was varied in order to produce paste viscosities which were essentially equal when measured at a temperature of 180° F. They were as follows: regular corn starch (Reg. PFP), 320 g.; pregelatinized, cross-linked waxy maize starch (HR W-13), 320 g.; starch phosphate (SPHV), 280 g.; and, ordinary all-purpose flour, 464 g. The hot viscosities of these white sauces ranged between 1300 and 1500 centipoises when measured with the Brookfield Synchro-Lectric Viscometer equipped with helipath stand.

Fat was liquefied by warming to about 140° F. in the steam-jacketed bowl of the mixer. Thickening agent was added and mixed thoroughly with the fat to form a roux, or smooth fat-starch mixture. Skim milk was preheated to 140° F. in a separate jacketed kettle. After the starch-fat roux had been prepared, the warm milk and salt were added to the mixture. The complete sauce was mixed for 20 minutes at medium speed. The dough beater attachment was used during the first 15

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minutes of mixing; the large whip for the last 5 minutes. Four p.s.i.g. steam pressure (225° F.) was maintained in the mixing bowl jacket. This resulted in a final product temperature of 185–190° F.

In addition a white sauce was prepared with Reg. PFP starch which was not allowed to gelatinize prior to freezing. The procedure was exactly as described above, except that instead of heating for 20 minutes, the total mixing time was 10 minutes and the sauce was maintained at a temperature of 140° F.

Each sauce was divided into 4 equal portions. The first of these was filled into Number 1 enameled cans, closed and placed in 0° F. storage. A second portion (about one quart) was placed in the laboratory homogenizer and allowed to recirculate for 5 minutes, during which time each increment of sauce received about 7 passes through the homogenizing orifice. The unit was operated at a pressure of 3500 p.s.i.g. since preliminary experiments indicated that an operating pressure greater than 2500 p.s.i.g. would be required to yield any improvement of freeze-thaw stability of white sauces. After homogenization, the sauce was canned and placed in 0° F. for freezing and storage.

A third portion of sauce was frozen directly in liquid nitrogen. Drops of white sauce were allowed to fall from a stainless steel spoon directly into a large Dewar flask containing liquid nitrogen (−196° F.). An effort was made to drop the sauce in such a manner that about ¼ in. diameter droplets would fall into the liquid nitrogen. After freezing, the sauce pellets were canned and placed at 0° F. Finally, a fourth portion was homogenized as for portion 2, then frozen in liquid nitrogen as for portion 3, canned and placed in storage.

Samples were stored for 0, 1, 7 and 14 days. The entire experiment was replicated 3 times. A 6-member taste panel evaluated samples for smoothness, liquid separation, mouth feel, flavor, and general acceptability. These factors were rated using a numerical scale of 1 to 5. Descriptive ratings with suggested scores were included on the score sheets to aid the panel and to improve the reliability of the testing. For example, in grading the factor of smoothness, very smooth homogeneous sauces were given a suggested rating of 5, while sauces exhibiting moderate graininess (20–80%) were rated 3 and very lumpy sauces were rated 1. Similar sets of descriptive terms for each major factor along with suggested numerical ratings from 1 to 5 were included on the taste panel score sheet. Taste panel data were subjected to a statistical analysis of variance using a single degree of freedom analysis *(7)*. Samples were also examined for "weeping" and enzyme susceptibility and the data similarly analyzed.

Post-thaw preparation of sauces for enzyme susceptibility analysis. After samples had been completely thawed, cans were opened and the contents placed in the mixing bowl of a small Kitchen Aid mixer. The mixer was operated on medium speed for 5 minutes, at the end of which time sufficient sample was removed to carry out the physical and chemical tests.

RESULTS AND DISCUSSION

Figure 1 shows pictures that are representative of the various white sauces encountered in this study. The terminology illustrated in this figure was used to summarize the appearance of the samples before and after freezing.

A comparison of the organoleptic data contained in Table 1 with results of enzyme susceptibility analyses (not shown) indicated that this chemical test was not a reliable criterion of undesirable changes occurring in frozen white sauces. For example, in the case of the control white sauce prepared with Reg. PFP starch (unhomogenized, no liquid nitrogen freezing treatment), the sample became very lumpy after freezing and storage as indicated by a drop in organoleptic smoothness score from 4.0 to 1.4 (Table 1). However, the corresponding enzyme susceptibility values for these two samples were 94 and 95, respectively, instead of showing a noticeable decrease as found for starch-water systems. This general lack of agreement was exhibited throughout.

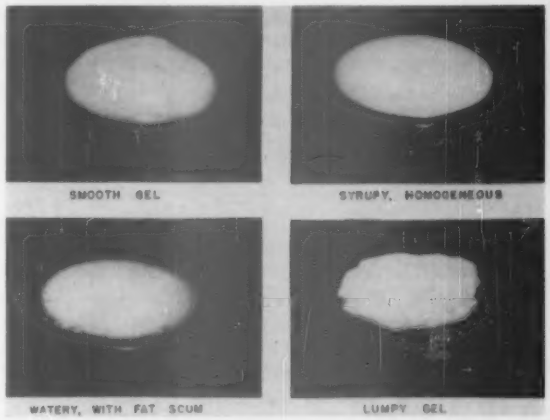

Figure 1. Photograph of white sauce samples after various treatments illustrating descriptive terminology in the text.

The failure of this test as an index of retrogradation when applied to white sauces may be ascribed to any one of the ingredients present in the sauce, excluding the thickening agent. The most likely explanation appears to concern the fat content of the sauce. Because the starch received an intimate mixing with the liquefied fat prior to the incorporation of other ingredients, it is probable that the fat formed a protective coating around the starch granule. Even with this coating, a certain amount of enzymatic action could be possible initially. However, retrogradation due to freezing and thawing might take place within the protective coating and remain undetected by enzyme susceptibility measurements.

The concentration of thickening agent in the white sauce was, in general, less than that used in studying the basic systems. Also, the enzyme susceptibility of all samples was much higher for sauces than for starch slurries. Therefore, one may also theorize that the other reducing substances present in the sauce overshadowed the changes occurring in the starch component, and thus made it impossible for such changes to show up in enzyme susceptibility data.

As indicated in the first paper of this series, enzyme susceptibility of a starch in suspension apparently is not a function of particle size, but is probably directly related to the porosity of the starch granule. This porosity would be changed by the molecular realignment occurring during retrogradation.

The complete statistical analysis of variance performed on the data from this storage study on frozen white sauce *(1)* is too lengthy for inclusion here. Only those single effects and interactions considered to be of greatest interest are shown in Table 2. The factors of mouth feel and enzyme susceptibility were omitted due to a general lack of significance. The mean square figures were omitted because the table is abbreviated and only the degree of significance is indicated in each case.

TABLE 1

Average taste panel scores for white sauces processed, frozen and stored at 0° F.

Thickening agent	Homogenization	Liquid N_2	Smoothness		Liquid separation		Mouth feel		Flavor		General acceptability	
			Days storage		Days storage		Days storage		Days storage		Days storage	
			0	14	0	14	0	14	0	14	0	14
			Average scores for three replications									
Reg. PFP	+	++	4.4	4.2	4.9	5.0	3.8	4.3	3.9	3.5	3.7	3.6
Reg. PFP	+	—	4.9	4.4	5.0	5.0	4.2	4.0	4.2	3.2	4.1	3.0
Reg. PFP	−	++	2.4	1.2	3.5	2.9	2.6	1.0	4.0	3.4	2.3	1.0
Reg. PFP	−	—	4.0	1.4	4.8	1.6	4.0	1.3	4.5	3.5	3.8	1.1
Reg. PFP[1]	+	++	4.3	4.8	4.9	5.0	3.2	2.8	3.8	3.3	2.5	1.9
Reg. PFP[1]	+	—	4.9	5.0	5.0	5.0	3.9	2.7	3.3	3.3	2.4	1.8
Reg. PFP[1]	−	++	3.8	4.2	4.9	5.0	3.1	2.6	3.0	3.0	1.9	1.6
Reg. PFP[1]	−	—	3.9	3.7	4.6	4.9	2.9	2.5	3.1	2.9	2.2	1.6
HR W-13	+	++	4.3	4.5	4.9	5.0	3.5	3.5	2.5	2.8	2.6	2.3
HR W-13	+	—	4.9	5.0	5.0	5.0	3.4	3.3	2.9	2.8	2.8	2.6
HR W-13	−	++	4.6	3.2	5.0	4.9	4.0	3.4	2.9	3.0	3.0	2.7
HR W-13	−	—	2.6	3.3	4.7	4.9	3.7	3.9	2.6	3.1	2.8	2.7
SPHV	+	++	4.2	4.4	5.0	4.8	4.7	4.7	4.2	3.2	4.3	3.8
SPHV	+	—	3.1	4.3	5.0	5.0	3.6	3.9	4.0	3.4	3.2	3.5
SPHV	−	++	4.2	3.9	5.0	5.0	4.2	4.4	3.0	3.3	3.3	3.4
SPHV	−	—	3.8	3.8	4.9	4.9	4.0	4.4	3.2	3.6	3.8	3.3
Flour	+	++	4.8	4.8	4.9	4.9	4.4	4.4	3.7	3.7	3.8	3.8
Flour	+	—	4.9	4.5	5.0	5.0	4.8	3.9	4.2	3.5	4.4	3.3
Flour	−	++	2.6	1.0	4.7	3.8	2.7	1.2	3.6	3.5	2.4	1.2
Flour	−	—	3.9	2.1	5.0	2.0	3.8	2.0	4.3	3.7	3.9	1.7

[1] Regular corn starch preheated to 145° F., and kept at this temperature for 10 minutes. Not pregelatinized.
+ Homogenized for 5 minutes at 3500 p.s.i.g.
— No homogenization treatment.
++ Frozen in liquid nitrogen prior to 0° F. storage.
— No liquid nitrogen treatment prior to 0° F. storage.

As may be seen in Table 2, the effect of storage was significant as a none vs. some relationship at the 1% level; a linear storage relationship was found to be significant at the 5% confidence level for all factors except smoothness and mouth feel. No significant quadratic effect was found for storage. Table 1 (thickeners 1 and 5) indicates that 14 days' storage at 0° F. adversely affected the stability of samples containing either pregelatinized Reg. PFP or flour. This finding was also in agreement with conclusions reached in earlier experiments with simple systems *(1a)*.

TABLE 2

Partial summary of statistical analysis of variance on organoleptic data from storage study of frozen standard white sauces

Factors and interactions	Smoothness	Liquid separation	Mouth feel	General accept.
D_1	**	**	**	**
D_2	—	*	—	**
B_1	**	**	**	**
B_1D_1	**	**	**	*
B_1C_1	—	*	**	*
A_1	**	**	—	**
A_1D_1	**	**	—	**
A_1B_1	**	**	**	*
$A_1B_1D_1$	*	**	**	**
A_2	—	**	**	—
A_2D_1	**	**	*	**
A_2B_1	*	**	**	**
$A_2B_1D_1$	—	**	**	*
A_3	—	*	—	**
$A_3B_1C_1$	**	—	*	**
A_4	—	**	**	*
A_4D_1	**	**	**	**
A_4C_1	**	*	**	**
A_4B_1	**	**	**	**
$A_4B_1D_1$	—	**	*	*

** Significant at the 1% confidence level. * Significant at the 5% confidence level. — Not significant.
D = storage (1 = some vs. none; 2 = linear relation).
B = homogenization (1 = homogenization for 5 minutes at 3500 p.s.i.g.).
C = freezing technique (1 = freezing in liquid nitrogen prior to 0° F. storage).
A = thickening agent (1 = pregelatinized vs. ungelatinized regular PFP; 2 = pregelatinized regular corn starch vs. HR W-13 + SPHV + flour; 3 = HR W-13 vs. SPHV and flour; 4 = SPHV vs. flour).

It was found that freezing in liquid nitrogen was not significant at the 5% confidence level. The fact that the liquid nitrogen technique in itself did not have a significant effect was in direct contrast to observations made with simple starch-water systems. In these simple systems, the more rapid the rate of freezing, the more stable the starch slurry. This complete reversal in observations is the first of several such notable variations between simple and complex starch systems.

The major differences in behavior between white sauces and basic starch-water systems are due to more than variations in formulation. To be sure, fat, skim milk, and salt each contributes to the complexity of the freeze-thaw stability problem. In addition, however, there exists an extremely complicated interaction between these factors. This situation makes it necessary to evaluate processing techniques directly on the complete formulated product under consideration, rather than on the simple starch slurry.

To further substantiate the above comments, it was shown that homogenization of pregelatinized Reg. PFP and flour samples for 5 minutes at 3500 p.s.i.g. produced white sauces noticeably superior to corresponding samples which had not received this treatment (Table 1). The same homogenization of simple starch-water systems had practically no effect on the freeze-thaw stability *(1a)*. The explanation for this reversal is not obvious. The presence of fat in white

sauces implies that homogenization may cause the smaller fat molecules to form a tighter and more uniform protective coating around the starch granules, thus making it more difficult for molecular alignment to take place during freezing and storage. It is apparent from data in Tables 1 and 3 that homogenization virtually created a new product, completely different in viscosity and freeze-thaw characteristics. While white sauces made with flour are ordinarily heavy and pasty, homogenization yielded a smooth product with a heavy syrup consistency, an ideal white sauce.

To facilitate statistical analyses, it was necessary to predetermine the method of comparison to be used for various thickening agents. Obviously essential was a comparison of pregelatinized versus ungelatinized Reg. PFP starch. The ungelatinized samples were quite watery after thawing (Table 3) but formed excellent white sauces when reheated to the boiling point. This confirmed earlier statements concerning the desirability of using ungelatinized regular corn starch in some products to be frozen.

Although taste panel scores in Table 1 indicated that acceptability of sauces made with ungelatinized Reg. PFP starch was poor, it was subsequently shown that these sauces could be made quite acceptable by post-thaw heating to gelatinize the starch. The use of ungelatinized regular corn starch as a thickening agent in precooked frozen foods is indeed limited to products which need not be in thorough suspension during frozen storage and which are reheated prior to consumption. A good example of such a product might be one of the frozen cream-style soups.

A second comparison of thickening agents was made between pregelatinized Reg. PFP systems and the other 3 types of thickening agents, HR W-13, SPHV, and flour. A significant difference at the 1% confidence level was obtained for the factors of mouth feel and liquid separation (Table 2).

The third comparison of thickening agents was made between HR W-13, starch phosphate and flour. Waxy maize, chosen because of its increasing acceptance as one of the more acceptable thickening agents for many precooked frozen foods, was generally inferior to starch phosphate (Table 1), but superior to flour.

A comparison of starch phosphate with flour resulted in significance at the 1% level (Table 2) for the factors of liquid separation and mouth feel. There was significance at the 5% level for the difference in general acceptability of the samples. Starch phosphate, because of its unusual freeze-thaw stability, offers promise of being one of the most acceptable of the newer starch derivatives for use in precooked frozen foods. Its properties of cold-water swelling, formation of high viscosity suspensions, clarity, and lack of typical starch taste all add to its desirability as a stable thickening agent for frozen foods.

SUMMARY

To determine the applicability of the findings on freeze-thaw stability of starch-water slurries, an investigation was carried out using standard white sauces prepared with regular corn starch, pregelatinized, cross-linked waxy maize starch, and starch phosphate. A control white sauce was also prepared using all-purpose flour as the thickening agent. Treatments of the white sauces included severe homogenization and freezing in liquid nitrogen. Using a six-member taste panel, samples were evaluated for smoothness, liquid separation, mouth feel, flavor, and general acceptability. Taste panel and enzyme susceptibility data were analyzed using a single degree of freedom statistical analysis of variance.

Storage was found to be significant at the 1% level in all cases with respect to some storage versus no storage. Freezing in liquid nitrogen was not statistically significant. Thus, there was no benefit to be de-

TABLE 3

Effect of thickening agent, homogenization and rapid freezing on the gross physical appearance of white sauces stored at 0° F.

Thickening agent	Homogenization	Liquid N_2	Gross physical appearance	
			Before freezing	After thawing
Reg. PFP	+	++	Syrupy; homogeneous	Syrupy; homogeneous
Reg. PFP	+	—	Syrupy; homogeneous	Syrupy, homogeneous
Reg. PFP	—	++	Slightly lumpy	Very lumpy; syneresis
Reg. PFP	—	—	Syrupy; homogeneous	Very lumpy; syneresis
Reg. PFP[1]	+	++	Watery	Watery
Reg. PFP[1]	+	—	Watery	Watery
Reg. PFP[1]	—	++	Watery; fat scum	Watery; fat scum
Reg. PFP[1]	—	—	Watery; fat scum	Watery; fat scum
HR W-13[2]	+	++	Light syrupy consist.	Light syrupy consist.
HR W-13[2]	+	—	Light syrupy consist.	Light syrupy consist.
HR W-13[2]	—	++	Syrupy; sl. lumpy	Syrupy; homogeneous
HR W-13[2]	—	—	Syrupy; sl. lumpy	Syrupy; homogeneous
SPHV	+	++	Syrupy; homogeneous	Syrupy; homogeneous
SPHV	+	—	Syrupy; homogeneous	Syrupy; homogeneous
SPHV	—	++	Syrupy; sl. lumpy	Syrupy; homogeneous
SPHV	—	—	Syrupy; sl. lumpy	Syrupy; homogeneous
Flour	+	++	Heavy syrup consist.	Too pasty
Flour	+	—	Heavy syrup consist.	Too pasty
Flour	—	++	Very pasty	Lumpy; syneresis
Flour	—	—	Very pasty	Lumpy; syneresis

[1] Preheated to 145° F. for ten minutes; not pregelatinized.
[2] Homogenized samples of HR W-13 sauces were considered to be too thin for white sauces.

rived by extremely rapid freezing of white sauces. This was in direct contrast to results obtained with starch-water systems.

On the other hand, it was shown that severe homogenization of white sauces prior to freezing significantly increased the freeze-thaw stability of these sauces; this result was again in direct contrast to results obtained with starch-water systems. However, it should be noted that these samples were not subjected to long storage periods, which might counteract the favorable effects of severe homogenization.

The enzyme susceptibility test was found to be unsatisfactory as an index of freeze-thaw stability of standard white sauce in contrast to the simple starch-water system. Furthermore, some techniques which greatly improved the stability of simple starch-water systems had little such beneficial effect on white sauces, while other processing treatments gave the opposite results. It was concluded from this that a complex relation exists between the thickener and other ingredients in a white sauce and that the thickening agent itself cannot be solely responsible for the curdled appearance of frozen white sauces.

Based on the results of investigations concerning both white sauces and starch-water systems, thickening agents were rated in decreasing order of freeze-thaw stability as follows: (1) starch phosphate, (2) ungelatinized regular corn starch (this technique is limited to products in which solids need not be suspended during freezing and storage and to products which are heated to near the boiling point before consumption), (3) pregelatinized, cross-linked waxy maize starch, (4) all-purpose flour, and (5) regular corn starch (which is gelatinized prior to freezing as part of the sauce formulation process).

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Of Professional Interest

Report on the Symposium Entitled "Symposium on Foods: Enzymes" Held at Oregon State College

A SYMPOSIUM ON FOODS: Enzymes, sponsored by the Department of Food and Dairy Technology of Oregon State College and the National Institute of Health was held at Corvallis, Oregon, September 9–10. Some 200 scientists from throughout the West attended and heard discussions on past accomplishments, the present status, and future research problems related to enzymes and their role in foods.

The enzyme symposium was one of the several symposia held on the Oregon State College campus in conjunction with the celebration of the Oregon Centennial. It was also held to honor Professor Ernest H. Weigand, retired head of the Oregon State College Food Technology Department, for his 40 years of service to the Oregon Food Industry.

H. W. Schultz, Head of the Food and Dairy Technology Department, said that this symposium was a beginning of symposia in food science to be held at Oregon State College. He also announced that papers presented at the symposium will be published in book form by the Avi Publishing Company.

Dr. E. M. Mrak, Chancellor and Professor of Food Technology, University of California, Davis, emphasized the importance of enzymes in the field of food science. Today enzymes are finding their proper place of importance in food research and it is recognized that while some may create undesirable effects in foods, others may be used to a great advantage, he said.

CLASSICAL PROBLEMS SOLVED BUT MANY REMAIN

Dr. David E. Green, Co-director, Institute for Enzyme Research, University of Wisconsin, discussed the future of enzymology. He pointed out that a foundation of the subject of enzymology was laid in the period prior to 1940 in Europe, but it was in this country during the '40's and '50's that enzymology skyrocketed from a pigmy to a giant dominating the field of biochemistry. The classical problems have been pared to the bone and many of the once flourishing frontier areas have become quiescent. The less spectacular but more difficult problems remain to be solved. Important unsolved problems for the enzymologist include the mechanisms of hormone action, oxidative phosphorylation, gene action, muscular contraction, protein synthesis, and the entire problem of biological organization.

Dr. Paul K. Stumph, Professor of Plant Biochemistry, Department of Biochemistry, University of California discussed the enzymes affecting food lipids. The importance of lipids as a food and as a means of storing energy and the known mechanisms for their degradation and synthesis were reviewed. The role of lipogenin as a new and important regulator in lipogenesis and the function of vitamins in lipid utilization by humans were stressed. Dr. Ralph T. Holman, Professor of Physiological Chemistry, University of Minnesota reviewed the mechanism of lipoxidase action on polyunsaturated fatty acids and the implications of such phenomena to the nutritive value and acceptability of foods. In no case has lipoxidase been demonstrated in animal tissue; rather, it is the catalytic activity of heme compounds present that is responsible for lipid oxidation in animal tissue in many instances. Mention was also made of recent findings in which the polyunsaturated fatty acids have been found to constitute a high percentage of the fatty acids in mitochondria and it was suggested that they may function as prosthetic groups of enzymes.

Dr. David R. Goddard, Director of the Division of Biology, University of Pennsylvania, emphasized the need for research on biological organization in his discussion of enzymes affecting oxidative browning. An example of this problem is the presence of large quantities of oxygen in plant tissue and it is not until some damage has resulted in the tissue that polyphenoloxidase catalyzes the formation of brown pigments.

Dr. James D. Ponting, Western Regional Research Laboratory, U.S.D.A., pointed out that the mechanism of polyphenoloxidase inactivation by sulfur dioxide has never been unraveled and that it is essential to know the oxygen content of fruit and vegetable tissue mentioned by Dr. Goddard in order to know the type of treatment necessary for preservation of the food. Other than sulfur dioxide, new methods involving heat inactivation appear promising for prevention of enzymatic browning, as do methods of controlling pH in the system. It was interesting to note that malic acid is more effective than citric acid in inhibiting the browning of apple juice. This was not attributed to a change in pH alone.

Dr. Vernon H. Cheldelin, Director, Science Research Institute, Oregon State College, described the pathways of carbohydrate degradation and synthesis including the most recent information of the Pentose Cycle. Dr. Z. I. Kertesz, Professor of Chemistry, Cornell University, pointed out that similar progress has not been made in describing the enzymes involved in the syntheses pathways for the formation of cellulose and pectins. Incorporation of simple glucose and galactose into the cellulose molecule is well recognized but the steps involved are not known. Methyl donors contribute methyl groups but again mechanisms for this reaction as well as polymerization steps are still to be determined. The danger of using substrates other than the native system for a particular cellulase

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test was pointed out. For example, the use of carboxymethylcellulose as a common substrate for a cellulase test may give dubious results.

ENZYME REGENERATION

Dr. A. J. Balls, Professor of Enzyme Chemistry, Purdue University, dealt with enzymes affecting proteins and the phenomenon of enzyme regeneration. In the process of heat denaturation, the denatured proteins are more susceptible to proteolysis. The enzymes also are denatured but not necessarily at the same rate. The total effect, therefore, on a food system is a matter of timing. The enzymes that stay undenatured longest can digest the less heat-resistant proteins and in the regeneration process the enzymes that revert most rapidly can hydrolyze the slower reverting food proteins. Caution should be taken in the development of high-temperature short-time equipment for food processing since foods treated in this manner may be more susceptible to enzyme regeneration, he said.

Dr. B. S. Schweigert, Director of Research and Education, American Meat Institute Foundation, discussed the importance of catheptic enzymes in aging and tenderization of meat. He also pointed out the value of using other proteolytic enzymes for the tenderization process. Aside from the problem of selecting the proper enzyme preparation, penetration and distribution of enzymes throughout the tissue is a critical factor in obtaining satisfactory results.

In summarizing the symposium, Dr. Mrak emphasized the need for greater cooperation between the different areas of scientific discipline. Greater exchange of ideas and knowledge, and the utilization of team effort will result in more rapid progress in the area of food science and technology.

PERSPECTIVES IN FOOD RESEARCH

The symposium was concluded by a look at the perspectives in food research by the late Dr. B. E. Proctor, Head (before his death on September 24, 1959) Department of Food Technology, Massachusetts Institute of Technology. Food research is now recognized as a factor of primary importance to all nations large and small, because of the population increases which are taking place all over the world. These population gains make food a factor of existence in some areas while in others it may be intimately connected with dreams of domination. Consequently, the importance of producing both quantity and quality of foods as well as assuring its delivery to the consumer in the most acceptable form are problems of immediate and continuing consideration to the food industry. A food researcher must not only stay abreast of the basic problems, but he must also be constantly cognizant of the changing attitudes, health, and well-being of the consumer. This may be summed up by saying that the consumer wants quality and convenience at a reasonable price. Enzymology will undoubtedly play an important role in providing the consumer with these requirements, he said.

IFT News

GREAT LAKES

One hundred twenty-seven members and guests of the Great Lakes Section, Institute of Food Technologists, enjoyed a very fine meeting at Fremont, Michigan, October 2, 1959.

The morning program consisted of a tour through the Fremont plant of the Gerber Products Corporation. The hour and a half tour covered the entire plant operation from raw product through processing, packaging, sterilization, labeling, casing, and warehousing. The membership was quite impressed and happy to have the opportunity to go through the Gerber Products Company plant.

Following a buffet luncheon at the Ramshorn Country Club, Mr. Ray Wakefield, Director of Research for Gerber's and National IFT President, discussed affairs of the Institute.

The afternoon technical program consisted of three technical papers; Dr. Howard Stier, Director of the Division of Statistics, National Canners Association, Washington, D. C., discussed "Statistical Quality Control and Its Importance in the Food Processing Industry"; Mr. L. Newsome, of the Continental Can Company, Chicago, Illinois, discussed, "Unusual Problems in Food Processing," and Dr. I. J. Pflug, Michigan State University, East Lansing, Michigan discussed, "Controlled Atmosphere Storage of Fruit."

The results of the election of 1960 officers were announced, and are as follows: Chairman, Joseph Adams; Vice-Chairman, I. J. Pflug; Treasurer, Paul A. Wolf; Secretary, Mary Morr; Executive Committee, C. R. Scott, R. C. Frodey; National IFT Council, F. J. Erickson.

FLORIDA

The Florida section got the 1959–60 season off to a good start with a two-day meeting October 2 and 3 on the University of Florida campus at Gainesville. Activities began with a well attended Executive Committee meeting Friday morning and continued through Friday and Saturday, ending with the Florida-Virginia football game Saturday afternoon.

An excellent program arranged by Dr. R. A. Dennison, Head of Food Technology and Nutrition Department of the University of Florida included a "Welcome" by Dean Brooker, College of Agriculture, University of Florida; "Food Research at Florida State University," Dr. H. Lewis, FSU; "Food Technology Research at University of Florida," Dr. R. A. Dennison; "Basic Studies on Unsaturated Fat Oxidation," Mr. Basil Tarladgis; "Lipid Oxidation in Fish," Mrs. Marelynn Zipser, FSU; "Variables Which Must Be Considered in Making Taste Panel Evaluations," Mrs. Alice Hodges, University of Florida; "Factors Influencing Fermentation in Three Systems of Bread Making," Mr. Charles Stone, FSU.

Following a business session Friday night we enjoyed the highlight of the two-day meeting, which was an address on "The Physiological Basis of Flavor" by Dr. Lloyd M. Beidler, Professor of Physiology at FSU.

The Saturday morning panel discussion "What Should Constitute the Food Technology Curriculum" moderated by Dr. R. A. Dennison created so much interest and discussion that the meeting carried on into the noon hour, most of the group forgetting all about the box lunches waiting. The discussions must have been interesting for this group to forget about eating. Panel members were Mrs. Virginia Allen, Director of Florida State High School Science Fairs; Dr. Aksel Olsen, Immediate Past President of IFT; Dr. W. R. Roy, Vice President Technical Services Division, Minute Maid Corporation; and Dr. A. H. Gropp, Professor of Chemistry and Assistant Dean, College of Arts and Sciences, University of Florida. They provided plenty of food for thought concerning the Food Technology Curriculum.

A barbecue at beautiful Lake Wauburg Friday afternoon contributed even more to a pleasant well rounded meeting. Certainly our group is off to a good start in the 1959–60 season.

INDIANA

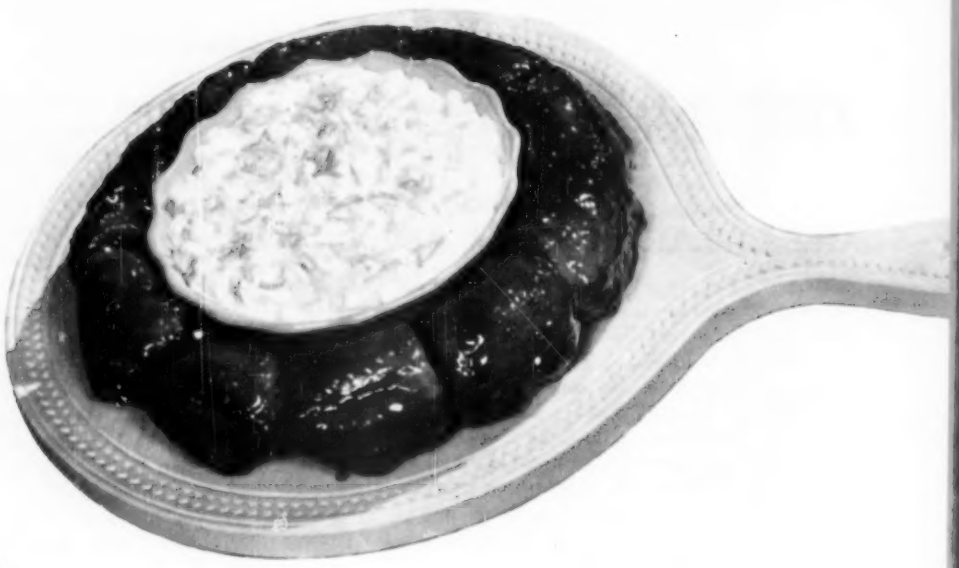
The Indiana Section's last meeting was held on Friday, January 8, 1960, at Turners Atheneaum, 401 East Michigan Street, Indianapolis, Indiana. The social hour at 5:45 E.S.T., followed by dinner at 6:30 E.S.T. Dr. I. J. Hutchings, President-elect of the National I.F.T., addressed the meeting, which is held in honor of the past chairmen of the section and their wives.

BY WAY OF REVIEW

The section's first meeting of the 1959–60 year was held at Turners Atheneaum. Mr. Samuel Alfend, Chief of the Cincinnati office of the Food and Drug Administration, discussed the new food additive amendment. Mr. Alfend pointed out the Administration's policy of firm and fair treatment for all. He invited the industrial representatives to come to their office and discuss common problems with them. All who attended were pleased to learn more about the additive amendment and to have Mr. Alfend as our guest.

The annual Purdue meeting was held November 13th at the Horticulture Building, Purdue University. The afternoon session was conducted by researchers at the University. Dr. W. J. Stadelman, Dr. C. E. Parmelee, Dr. G. E. Vail, Dr. N. W. Dearosier, and Dr. S. E. Hartsell discussed current interest in their various areas.

The evening session was held at the Fowler Hotel. Dr. Erich L. Clitheroe of the Department of History,



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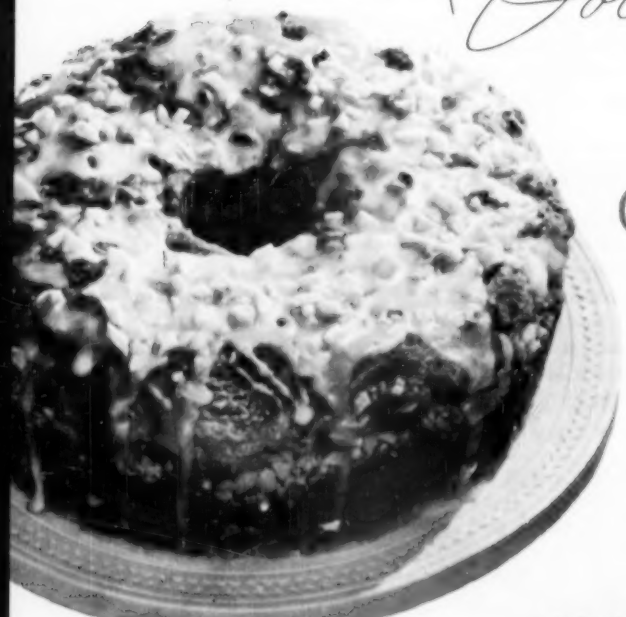

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Government and Philosophy at Purdue discussed Food Health and Politics in the Far East.

The section is planning two other meetings in this current series, the first on Monday, March 21, 1960, and the second on Tuesday, May 10, 1960, at the Turners Atheneaum. The social hour will begin at 5:45 E.S.T. with dinner at 6:30 E.S.T.

S. CALIFORNIA

The annual Food Man of the Year Award was presented posthumously to Dr. Ernest Geiger at the November meeting of the Southern California Section on Wednesday, November 18, in Los Angeles. Mrs. Lilly Geiger accepted the award from Chairman Henry Espoy who reviewed Dr. Geiger's many accomplishments in food and nutrition research during his long association with Van Camp Sea Food Company.

Dr. Milo Don Appleman, Head of the Department of Bacteriology, University of Southern California, and long time friend of Dr. Geiger, gave the feature talk of the evening on the subject "A Few Problems of Food Spoilage, Infection and Intoxication."

Toxicity problems associated with certain fishes, such as mussels, rays, sea bass, etc., were discussed. Food poisoning resulting from bacterial spoilage due to *Clostridium perfringens* has been recently reported in this country. The probability of similar outbreaks in frozen meat pies and TV dinners were suggested since many processing plants hold these products too long in a temperature zone of 25° to 40° C.

Staphylococci food poisoning is the most common type and accounts for about 1,500 cases each year in California. Better food handling controls are needed to cut down this type of intoxication. Salmonella infection, as distinguished from intoxication, resulting from food contaminated by a carrier is also a present danger.

Dr. Appleman's talk was well received by the membership.

—E. Kyle Bacon

OHIO VALLEY

Our first meeting of the year was held October 15 in Silverton in the "Stube" of Meier's Wineries. President Radcliffe Robinson called upon Secretary Wilbur Gould for a brief history of the Ohio Valley Section as part of a program to recognize the 10th Anniversary of its founding. Dr. Gould reported on the first meeting of the Ohio Valley Association of Food Technologists which was held in Cincinnati, Ohio on October 10, 1946 with Dr. H. D. Brown of Ohio State University as guest speaker. The officers were R. A. Wait, President, N. H. Volle, Vice President, and S. H. Champlin, Secretary-Treasurer. Subsequent meetings were held in Columbus, Cincinnati, Dayton and Louisville. At the February 5, 1949 meeting in Columbus, 105 persons were in attendance and the following persons were appointed to organize the Ohio Valley Section of IFT: H. J. Alleman, K. S. Chester, D. C. McCoy, R. J. Ridenour, N. H. Volle, with F. H. Dellwo, Chairman. This Committee drafted the following petition and submitted same to the May 21, 1949 meeting of this Association in Louisville, Kentucky.

> "Believing ourselves to be duly qualified and worthy of consideration, the undersigned hereby petition the Committee on Regional Sections of the Institute of Food Technologists that a Regional Charter be granted us. We wish to be known as the Ohio Valley Section of the Institute of Food Technologists with headquarters in the city of Cincinnati, Ohio and boundaries extending therefrom to include the states of Indiana and Ohio, south of U. S. Highway No. 30, and the state of Kentucky. . . . We agree to support the aims of the Institute of Food Technologists as set forth in its Constitution. We further agree to conduct our affairs in a manner prescribed by the Institute of Food Technologists Constitution as it now exists, or as it shall be amended from time to time. Respectfully submitted this 21st day of May, 1949, Chairman, N. H. Volle; Vice-Chairman, H. D. Brown; Secretary-Treasurer, Dan Ridenour."

In addition to the above officers, 25 National Members of the Institute of Food Technologists signed the petition. This petition was submitted to the National Committee on Regional Sections at the Palace Hotel in San Francisco on July 9, 1949. The 39 Councilors

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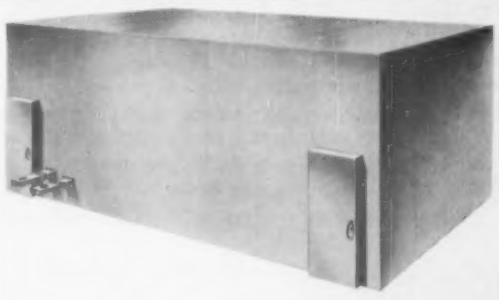

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in session accepted the petition of the Ohio Valley Section as Regional Section No. 15. The first meeting of the New Section was held on October 10, 1949. Then President Robinson presented framed certificates to all of the past presidents of the Section, and introduced those who were present, including Florren Long, W. A. Gould, G. F. Garnatz, and N. H. Volle. Tribute was paid to past president and councilor H. D. Brown who died on September 29, as all present stood for a moment of silence.

The three speakers for the evening each presented viewpoints on the topic, "The Effect of the St. Lawrence Seaway on the Food Industry In Ohio." Mr. Robert C. Haldeman from the Transportation Section of the USDA in Washington explained briefly the physical facilities of the Seaway, the effect it is expected to have on industry and commerce in Ohio and the midwest, mentioned a number of commodities that are presently being transported via the Seaway, emphasizing that it will exert a very marked effect on all industry in this part of the country. Mr. J. Bert Moher of Inland Forwarding Company pointed out that the Seaway has put the interior of the United States in a new and favorable position for shipping to Western Europe. In the case of food processors located reasonably close to Toledo, for example, they are as favorably located now as are processors in the metropolitan New York City area. Both speakers also pointed out that the same factors that tend to lower *export* costs also have a similar effect upon *import* costs, so in certain instances foreign goods can now come into the Ohio Valley more advantageously than in the past. Dr. Gould had just returned from a month's trip to Germany and Italy where he participated in a large International Food Exposition in Cologne, and a symposium on frozen foods in Italy. He emphasized very strongly that conditions now are very favorable for the introduction and promotion of American foods in Western Europe as a result of the poor food crops there this year, and the fact that Europeans seem to be accepting and liking American foods more and more. Dr. Gould, as well as the other two speakers, placed strong emphasis on the idea that great possibilities exist right now for American Food processors, and particularly those in this area close to the Seaway, to explore and develop a relatively new and undeveloped market for American foods.

—Norman Spain

NORTHEAST

The speaker for our second meeting, November 17, was Nathaniel Brenner, Manager of Applications Engineering, The Perkin-Elmer Corporation, Norwalk, Connecticut. Mr. Brenner is Manager of the Applications Engineering Department of the Instrument Division of The Perkin-Elmer Corporation, Norwalk, Connecticut. Prior to his appointment as Manager of Applications Engineering, he was the Gas Chromatography Product Specialist for this department. Before joining Perkin-Elmer, he was a spectroscopist at the Naval Air Experimental Station at Philadelphia. Mr. Brenner received his B.S. in chemistry in 1948 from Queens College, Flushing, New York.

Our December 15th meeting was Ladies' Night. Nancy Carter, of the Sheraton Corporation, Boston, spoke on "Food Technology in the Hotel Industry."

Committees. Chairman Anderson is pleased to announce that the following members have agreed to serve as chairmen of our various committees:

Auditing—S. A. Goldblith, Dept. of Food Technol., M.I.T.

Budget—J. T. R. Nickerson, Dept. of Food Technol., M.I.T.

Employment—L. V. Taylor, William Underwood Co., Watertown, Mass.

Hospitality—Co-chairman, J. Licciardello, Dept. of Food Technol., M.I.T.; Co-chairman, Miss J. Tichenor. Flavor Lab., Arthur D. Little, Inc.

Membership—F. J. Francis, Dept. of Food Technol., University of Massachusetts.

Program—W. B. Esselen, Dept. of Food Technol., University of Massachusetts.

Your committee chairmen and your section officers stand ready to answer questions, accept constructive criticism or praise relative to the operation of the Northeast Section of IFT.

—E. P. McFee

ST. LOUIS

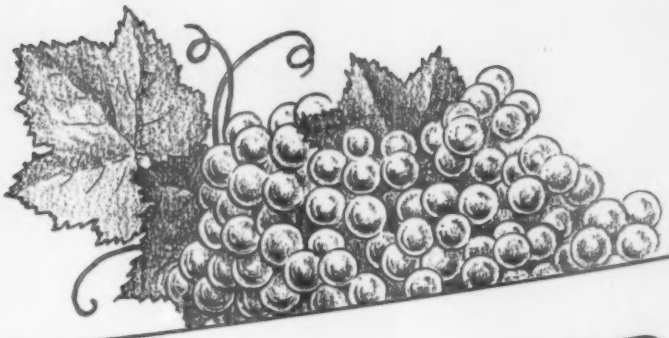
On November 6th the members of the St. Louis Section were presented with a talk entitled "New Developments in the Application of Gums and Stabilizers to the Food Industry" by Mr. Leonard Waldt, Chief Food Chemist for Morningstar-Paisley, Inc. Mr. Waldt's extensive experience in this field, particularly in the Brewing Industry, made the talk very interesting.

During the business section of the meeting the forthcoming Food Technology Short Course at the University of Missouri was discussed. This Short Course is sponsored jointly by the St. Louis Section, the Kansas City Section, and the College of Agriculture of the University of Missouri. It will be held March 11 and 12 and the theme will be the "Impact of Convenience Foods on Processing, Packaging, and Customer's Acceptance."

—L. J. Ahlberg

CHICAGO

Chicago Section IFT'ers took advantage of the combined meeting with the Wisconsin IFT Section in Madison to attend the Wisconsin-Stanford Football Game, and saw Wisconsin win the game in a close contest. Before the game, an excellent tour of the University of Wisconsin's Department of Dairy and Food Industries facilities was conducted and enjoyed by all who made the trip to Madison.



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Our many thinks to the Wisconsin Section and to those who arranged the day's activities. Also our appreciation to Dr. Ken Weckel and his associates in the Department of Dairy and Food Industries for their part in making the day a success, and for a job well-done.

In spite of the "heavy dew" beginning in the second half of the game, a wonderful time was had by all.

BRITISH COLUMBIA

The first meeting of the season for the B. C. Food Technologists and the B. C. Section Institute of Food Technologists was held at McGavin's Bakery Auditorium on October 22nd. Mr. Henry Murdy and Mr. Reg. Boltar officiated. Members and friends were very enthusiastic about the papers which were on various phases of the meat-packing industry. As the first speaker Mr. Don MacKinnon, chief chemist of Burns and Company Ltd. Vancouver plant, developed points concerning the work of the chemist in the industry. He pointed out how many of the by-products such as tallows and inedible oils are now finding competition from the synthetics and how they as a company support fundamental research through the American Meat Institute Foundation at the University of Chicago. Don's work includes controlling of various additives, checking the various operations in the plant and working with government inspectors to ensure optimum sanitation and cleanliness throughout the plant.

Mr. Ray Gayton, food technologist and supervisor at Canada Packers, Ltd., told us of their problems in bringing livestock from producing areas such as Calgary, Lethbridge, Edmonton, Peace River, and Williams Lake. Present regulations require that cattle and hogs be removed every 36 hours for watering and feeding and therefore the utmost is done to get the animals to the packing house in less than the 36 hour period. Ray also discussed newer techniques used throughout meat plants and the various problems of the industry which include the long 15–20 day holding time necessary with pork products.

Mr. Bill Smith, senior supervisor and chemist at Canada Packers Ltd. Vancouver plant, told us of the complexities of the meat packing industry. He pointed out how the basic products obtained from cattle now include such end products as gelatin, neatsfoot oil, pharmaceuticals etc. In their diversification from meat packing they are now in the canning, feed, tanning and frozen food industry. In the research and laboratory work they divide into groups working on new, faster determinations, oil and shortening work, meats, bacteriological, biochemical and development. All this leads to cheaper, safer and tastier meat products.

—C. E. Bullen

PERSONNEL

Lloyd A. Hall has been named to the Truesdail Laboratories' research advisory board, it was announced by Dr. Roger W. Truesdail, president of the well-known west coast independent research firm. Well known for his work on meat curing products, seasonings, emulsions, bakery products, antioxidants, protein hydrolysates and for unusual processes for sterilization of spices, cereals and other products, Dr. Hall will be called into consultation on unusual food or drug research projects requiring highly specialized knowledge. A graduate of Northwestern University, Dr. Hall is holder of three honorary degrees, author of some 40 professional papers, and patentee or co-patentee of more than 100 patents. Recently Dr. Hall moved to Pasadena, California, from Chicago, where he has been technical director of the Griffith Laboratories.

FUTURE MEETINGS FOR FOOD TECHNOLOGISTS

1959-1960	
January 17-20	Canners Convention and Show, Americana Hotel, Bal Harbour, Florida
January 18-20	National Canners Association 53rd Annual Convention, Miami Beach, Florida
February 11-13	National Food Conference, Palmer House, Chicago, Illinois
February 12-14	Fact Finding Conference, Institute of American Poultry Industries, Kansas City, Missouri
February 23-24	Eighth Annual National Dairy Engineering Conference, Kellogg Center, Michigan State University, East Lansing, Michigan
March 3-4	Second Better Foods for Better Nutrition Conference, Center for Continuing Education, University of Georgia, Athens, Georgia
March 11-12	Eighth Annual Food Technology Short Course, "Impact of Convenience Foods," Memorial Student Union, University of Missouri. Sponsored jointly by the St. Louis and Kansas City Sections of IFT with the College of Agriculture, Columbia, Missouri
April 19-21	Research and Development Associates 14th Annual Meeting, Congress Hotel, Chicago, Illinois
1960	
May 15-19	**Twentieth Annual Meeting of the Institute of Food Technologists, Fairmont Hotel and Masonic Temple, San Francisco, California**
May 19 to May 25 or 29	**IFT Pacific Rim Conference, Princess Kaiulani Hotel, Honolulu, Hawaii**
1961	
May 7-11	**Twenty-first Annual Meeting of the Institute of Food Technologists, Hotel Statler, New York, New York**
1962	
June 10–14	**Twenty-second Annual Meeting of the Institute of Food Technologists, Fontainebleau Hotel, Eden Roc Hotel, Miami Beach, Florida**
1963	
May 19–23	**Twenty-third Annual Meeting of the Institute of Food Technologists, Pantlind Hotel, Civic Auditorium, Grand Rapids, Michigan**

An open invitation is extended to readers of FOOD TECHNOLOGY to send in to the Editorial Office, 11406 South Bell Avenue, Chicago 43, Illinois notices of annual or national meetings of interest to food technologists.

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Literature

BOOKS

COLORIMETRIC METHODS OF ANALYSIS INCLUDING PHOTOMETRIC METHODS. Volume IIA. Foster Dee Snell, Cornelia T. Snell and Chester. D. Van Nostrand Company, Inc., Princeton, New Jersey, 1959, 793 pages, 32 illust., $15.00.

This new addition to the various editions of COLORIMETRIC METHODS OF ANALYSIS first authored by Dr. Foster Dee Snell in 1921, constitutes a supplement to Volume II of the third edition, which dealt with the Inorganic Methods, Colorimetric and Photometric. The present volume covers new colorimetric and flame photometric methods for inorganic analysis which appeared from the date of publication of the third edition's Volume II to January 1956.

The book comprises 68 chapters, each one devoted to the determination of one or more metallic or non-metallic elements, anions or compounds. Methods for carbon, carbon monoxide, dioxide, carbonates, cyanide, cyanate and alpha-hydroxy-nitriles are included.

Each chapter is prefaced by a short summary highlighting the analytical developments detailed in it.

Among the methods cited in the book, are many of value to the food scientist. Numerous chapters include procedures for carrying out determinations on tissues, foodstuffs, biological materials and/or other samples of organic origin.

The wealth of methodology included, the clearness, conciseness, yet completeness of presentation, the selective usage of tables and line drawings where needed, and the careful annotation of the methods to journal references render this volume indispensable to any up-to-date food science library.

G. E. LIVINGSTON
New York, N. Y.

LITERATURE ON FOOD RESEARCH AND TECHNOLOGY[a]

Commodities

Potato flakes; a new form of dehydrated mashed potatoes. IV. Effects of cooling after precooking. J. Cording, J. F. Sullivan, and R. K. Eskew. Washington, 1959. 26 p. (U.S.D.A. Agricultural Research Service. ARS 73-25.) apply.

Principles of sugar technology. v. 2. *Crystallization.* Pieter Honig. Princeton, N. J., Van Nostrand, 1959. 585 p. $19.00. An Elsevier Press production.

[*Production of essential oils.*] Teknologiia efiromaslichnogo proizvodstva. N. P. Skol'nikov and A. P. Kondratskii. Moscow, Pishchepromizdat, 1958. 201 p.

United States standards for grades of canned grapefruit. Washington, U.S.D.A. Agricultural marketing service, 1959. 6 p. Apply. Standards effective November 6, 1959, superseding those of January 19, 1954. First published in the *Federal Register* November 6, 1959.

Food Technology

[*Preparation of food.*] Prigotoviesoie pishchi. P. D. Griskin. Leningrad, Lenizdat, 1959. 450 p.

[*Refrigerating machines and installations.*] Kholodil'nye machimy i sooruzheniia. N. V. Dem'iarnkov and V. A. Abramov. Moscow, Gos. Transp. Zhel-dor. izdvo, 1959. 434 p.

Technology of food preservation. Norman W. Desrosier. Westport, Conn., Avi Publ. Co., 1959. 432 p. $8.50.

Some aspects of food technology in India. ed. H. A. B. Parpia, R. C. Bhutiani, K. L. Radhakrishnan, A. N. Sankaran, and B. V. Subbarayappa. Central Food Technological Research Institute, Mysore, India.

Nutrition

An experimental inquiry into the principles of nutrition and the digestive process. John R. Young. Urbana, University of Illinois Press, 1959. 74 p. (Facsimile reprints in the history of science, no. 1.) $2.50. Facsimile of a thesis presented to the Medical Faculty of the University of Pennsylvania on June 8, 1803, and overlooked for nearly 100 years before its importance was recognized.

Food guide for older folks. U. S. Institute of Home Economics. Washington, 1959. 16 p. (U. S. D. A.: Home and garden bulletin 17, rev.) apply.

Heinz handbook of nutrition; a comprehensive treatise on nutrition in health and disease. New York, McGraw-Hill, Blakiston Division, 1959. An H. J. Heinz' publication with a detailed explanation of the body's use of food.

Principles of nutrition. E. D. Wilson, K. H. Fisher, M. E. Fuqua. Wiley, 1959. 483 pp. $5.95.

Biological and Chemical Aspects

Annual review of microbiology, v. 13. Charles E. Clifton and others, eds. Palo Alto, Cal., Annual Reviews, 1959. 560 p. $7.00.

Biochemistry of blood in health and disease. I. Newton Kugelmass. Springfield, Ill., Charles C. Thomas, 1959. 554 p. (American lectures in living chemistry, no. 348.) $15.75.

Physico-chemical properties of proteins with special reference to wheat proteins; comprising papers read at a Symposium organized by the Food Group held at 14 Belgrave Sq., London, 27 March 1957. New York, Macmillan, 1959. 95 p. (Society of Chemical Industry. Monograph no. 6.) $2.00. A total of seven papers.

Principles of dairy chemistry. Robert Jenness and Stuart Patton. New York, John Wiley, 1959. 454 p. $8.75. Authors are at the University of Minnesota and Pennsylvania State University.

Miscellaneous

The canning industry. Nelson A. Budd. Cambridge, Mass., Bellman Pub. Co., 1959. 36 p. (Vocational and professional monographs, no. 99.) pap. $1.00. Another of the vocational guides which deal with various professions in the food industry.

Mechanically processing wholesale frozen food orders. T. H. Allegri and R. R. Bogardus. Washington, 1959. 20 p. (U.S.D.A. Agricultural Marketing Service. AMS-317.) pap. apply.

Special rations for the armed forces, 1946–53. Franz A. Koehler. Washington, Historical Branch, Office of the Quartermaster General, 1959. 377 p. (QMC Historical Studies, Series II, no. 6.)

[a] Material for this list should be sent to Dr. James G. Hodgson, Chief, Library Branch, Quartermaster Food and Container Institute for the Armed Forces, 1819 W. Pershing Road, Chicago 9, Illinois.

ABSTRACTS

General Foods Research Center
Selected by H. A. Campbell

ANALYTICAL METHODS

Paper chromatography of the saturated fatty acids.

BUCHANAN, M. A. (Inst. of Paper Chem., Appleton, Wisc.). *Anal. Chem. 31*, 1616–18 (1959).

In a new procedure for the paper chromatography of the satd. fatty acids, the developer reacts with the unsatd. acids to form products which readily sep. from the satd. acids. Hydrogen peroxide and formic acid are added to the usual acetic acid-water developers used for reverse-phase chromatography of the fatty acids. The new procedure permits the sepn. of small amts. of satd. acids from large amts. of the unsatd. acids, and is suitable for tentative identification of the even-numbered straight-chain acids from lauric acid to lignoceric acid.

Detection of trace constituents by gas chromatography.

FARRINGTON, P. S., PECSOK, R. L., ET AL. (Univ. of California, Los Angeles). *Anal. Chem. 31*, 1512–16 (1959).

Apparatus and techniques are described which are applicable to the detailed analysis of polluted atmospheres, including the detection and detn. of components present in the range of a few p.p.m. Important features are the sample handling technique and the ion gage detector.

BIOLOGICAL SCIENCES

Biochemisty

Determination of free lysine ε-amino groups in cottonseed meals and preliminary studies on relation to protein quality.

BALIGA, B. P., BAYLISS, M. E. AND LYMAN, C. M. (Texas Agr. Expt. Sta., College Station). *Arch Biochem. Biophys. 84*, 1–6 (1959).

A procedure is described for the detn. of free lysine ε-amino groups in cottonseed meal. In preliminary tests, a relationship was found between the content of lysine with free ε-amino groups and protein quality as detd. in rat protein repletion tests.

Chemical specificity in biological systems.

KAUZMANN, W. (Princeton Univ., N. J.). *Revs. Modern Physics 11*, 549–56 (1959).

Some typical examples of biological specificity involving more or less well-defined chemical systems as one of the specific interacting agents are considered in this paper, e.g. antibody-antigen interactions; enzyme-substrate interactions and the binding of small molecules to proteins.

Mechanisms of enzyme inhibition by phosphate esters.

BERNHARD, S. A. AND ORGEL, L. E. *Science 130*, 625–6 (1959).

A theory for the rapid specific reaction of certain phosphorus-contg. esters with many proteolytic enzymes based on the ability of phosphorus to form one addnl. bond relative to carbon is presented. A pentagonal enzyme-carbonyl substrate complex is assumed to be the transition state in the enzyme-catalyzed reaction.

Essential groups of porcine pancreatic amylase and of taka amylase. Acetylation with acetic anhydride.

RADICHIEVICH, I., BECKER, M. M., ET AL. *J. Am. Chem. Soc. 81*, 2845–51 (1959).

The results of this investigation show that porcine pancreatic amylase and taka amylase both require free primary amino groups for their catalytic action. Moreover, in both cases, the α-amino groups of the protein appear to be of more importance in this respect. Thus, these 2 α-amylases resemble each other and differ from β-amylase in the active groupings needed for their biological action.

Theory of the phase transition between helix and random coil in polypeptide chains.

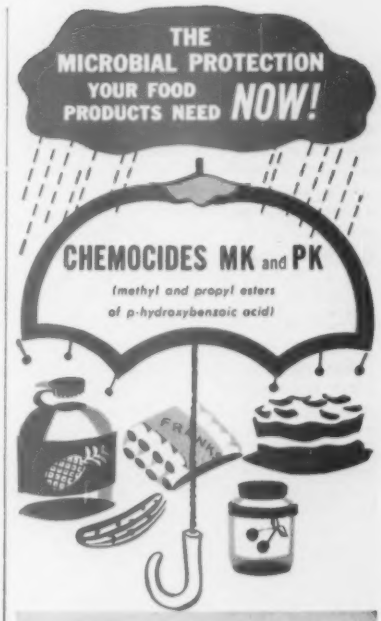
ZIMM, B. H. AND BRAGG, J. K. (General Electric Co., Schenectady). *J. Chem. Phys. 31*, 526–35 (1959).

The transition between the helical and randomly coiled forms of a polypeptide chain is discussed by reference to a simple model that allows bonding only between each group and the third preceding. Two principal parameters are introduced, a statistical parameter that is essentially an equilibrium const. for the bonding of segments to a portion of the chain that is already in helical form, and a special correction factor for the initiation of a helix. Depending on the values of the bonding parameter and the chain length, one of the following configurations dominates: random coils, single helices with occasional disorder at the ends, and for longer chains, helices occasionally broken by random sections.

Preliminary studies on the degradation products of quercetin in the rat's gastrointestinal tract.

KALLIANOS, A. G., PETRAKIS, P. L., ET AL. (Univ. of Okahoma, Norman). *Arch. Biochem. Biophys. 81*, 430–3 (1959).

Radioactive phloroglucinol carboxylic acid, phloroglucinol and protocatechuic



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acid were identified by paper chromatographic studies of exts. of lyophilized rat stomach and its contents following feeding of quercetin-C^{14}. A fourth radioactive compd. still unidentified plus a radioactive "quercetin-like" compd. were also noted.

Unique luminescence of dry chlorophylls.

BECKER, R. S. (Univ. of Houston, Texas). *J. Chem. Phys. 31*, 467–72 (1959).

Dry chlorophylls *a* and *b* in a rigid glass hydrocarbon solvent have intense emission at 7550 A and 7330 A, resp. In each case, the room temp. absorption spectra show the presence of a band shoulder on the long wavelength side of the main red band. Both the emission and the absorption bands disappear in the presence of hydroxylic solvents. Cu chlorophyll *b* has an intense phosphorescence at 8740 A with a lifetime of less than 10^{-4} second.

Effects of thyroid and adrenal cortical hormones on restoration of liver protein and enzyme activity after partial hepatectomy in rats.

TIPTON, S. R., MAJORS, C. W. AND SMOTHERS, J. L. (Univ. of Tennessee, Knoxville). *Am. J. Physiol. 197*, 71–4 (1959).

Propylthiouracil depressed and thyroxine elevated the succinoxidase activity of rat liver after 4 days of regeneration. Protein-depleted animals had a significant decrease in activity of succinic dehydrogenase and cytochrome oxidase, rate of restoration of liver mass, enzyme activity and new protein. Thyroxine increased the rate of regeneration and the enzyme activity even in protein-depleted animals. These hormones can produce changes in specific enzyme proteins that are independent of changes in total cell protein.

Microbiology

Survival of Clostridium tetani.

MURRAY, T. J. (Rutgers Univ., New Brunswick, N. J.). *J. Bacteriol. 78*, 293–4 (1959).

Thirty-four strains of *C. tetani* in brain heart agar in test tubes, sealed in 1930, were viable and gave typical growth and spore formation in February 1959.

Acquisition of lactose-fermenting properties by salmonellae. I. Interrelationship between fermentation of cellobiose and lactose.

SCHAFLER, S. AND MINTZER, L. (Dr. I. Cantacuzino Inst., Bucharest, Romania). *J. Bacteriol. 78*, 159–63 (1959).

A close relationship exists between the fermentation of lactose and cellobiose by salmonellae. Lactose-pos. variants acquire the property of fermenting cellobiose. Fermentation of lactose may be obtained more readily following previous inoculation in cellobiose. Lactose-pos. variants can be obtained by this method in 55 of the 56 salmonella strains studied. The cellobiose-pos. population varies with the formation of lactose-pos. salmonellae.

Bacterial species of the rumen.

BRYANT, M. P. (U. S. Dept. of Agr., Beltsville, Md.). *Bacteriol. Revs. 23*, 125–53 (1959).

This review is limited to pure culture studies with emphasis on the species of bacteria cultured. 132 references.

Psychrophilic bacteria.

INGRAHAM, J. L. AND STOKES, J. L. (Univ. of California, Davis). *Bacteriol. Revs. 23*, 97–108 (1959).

Psychrophiles have been defined as bacteria which grow appreciably and often abundantly at 0° C. for 2 weeks. These bacteria are ubiquitous, can be isolated, sometimes in large numbers, from soil, air, fresh and salt water, common foods, and other habitats, and are important spoilage organisms in meats, poultry, fish and dairy products stored at 0° C. 64 references.

The most poisonous poison.

LAMANNA, C. *Science 130*, 763–72 (1959).

An outline of some of the current knowledge of the nature of the botulinal toxin with questions of interest to be answered.

Metabolic injury to bacteria at low temperatures.

STRAKA, R. P. AND STOKES, J. L. (Western Regional Research Lab., Albany, Calif.). *J. Bacteriol. 78*, 181–5 (1959).

Metabolic injury to bacteria at subzero temps. has been demonstrated with several species of the genus *Pseudomonas* and with *Escherichia coli*. Cold injury is manifested by an increase in nutritional requirements. The injured cells can no longer grow on a simple, glucose-salts agar medium but can develop on a rich, complex medium trypticase soy agar. Injured cells may constitute as much as 40% of the bacterial population.

Nutrition

The utilization of marine algae in tropical south and east Asia.

ZANEVELD, J. S. (Caribbean Marine Biol. Inst., Curacao, Netherlands Antilles). *Econ. Bot. 13*, 89–131 (1959).

The algae have come to be regarded as very important in the future economy of a crowded world. The literature on the economic application of about 75 species and varieties of algae is reviewed. The material is arranged alphabetically for the benefit of non-botanists. 160 references.

Nutrition and disease: Folic acid deficiency in the mouse.

GRIGGS, G. M. (U. S. Dept. of Health, Educ. and Welfare, Bethesda, Md.). *Am. J. Clin. Nutrition 7*, 390–6 (1959).

An uncomplicated deficiency of folic acid was produced in young mice by feeding them a synthetic diet low in folic acid contg. 20% casein, 8% gelatin and 0.8% methionine. Further preliminary studies indicated that the folic acid deficiency might also be produced if 1.7% glycine were substituted for the gelatin. Evidence was obtained that the folic acid deficiency delayed the time of death when the mice were subjected to infections by the virus or lymphocytic choriomeningitis and certain transplantable lymphocytic neoplasms.

The uses of recommended dietary allowances in military nutrition.

FRIEDEMANN, T. E., KRAYBILL, H. F. AND CONSOLAZIO, C. F. *Am. J. Public Health 49*, 1006–12 (1959).

The feeding of U. S. Army personnel is planned in accordance with minimal dietary standards which are based upon the recommended dietary allowances of the Natl. Research Council, as modified by the special requirements of troops under various operational conditions. Standard minimum intake of the phys. active soldier in a temperate climate is: 3,600 calories, 100 g. protein, 700 mg. calcium, 5,000 I.U. vitamin A, 75 mg. vitamin C, 1.7 mg. thiamine, 2.0 riboflavin, and 16 mg. niacin.

The 1958 revision of recommended dietary allowances.

SHANK, R. E. *Am. J. Public Health 49*, 1001–5 (1959).

A description of changes that have been made in the fourth edition of Recommended Dietary Allowances. The author presents the nature of the changes and discusses their implications.

Biological availability of amino acids in fish meals and other protein sources.

OUSTERHOUT, L. E., GRAU, C. R. AND LUNDHOLM, B. D. (Univ. of California, Davis). *J. Nutrition 69*, 65–73 (1959).

A new chick assay method is proposed for the estn. of essential amino acids available to the animal from various protein sources. The material to be tested

is fed as a supplement to a diet replete with cryst. forms of all essential amino acids except the one being studied; thus the source supplies this one as well as non-essential amino acid needs. The growth response to this diet, compared with that for the same diet plus the missing amino acid, allows estn. of the amino acids furnished by the protein source. Results of tests with 19 protein sources are given for a number of amino acids, with special emphasis on fish meals of variable and known histories.

Diets of post-adolescent young women.

FRY, P. C. (Forsyth Dental Infirmary for Children, Boston, Mass.). *J. Am. Med. Assoc. 35*, 687–91 (1959).

An evaluation was made of the mean daily intakes of 12 nutrients for a group of 144 young women, aged 18 to 25 years. Only 35% had caloric and thiamine intakes of 90% or more of the Recommended Dietary Allowances, while the protein intake of 44% of the subjects was below this level. It was found that 84% of the Ca intakes, 83% of the Fe intakes, 25% of the vitamin A intakes, 31% of the ascorbic acid intakes, 58% of the riboflavin intakes, and 34% of the niacin intakes were below this level.

Relationship between plasma amino acids and composition of the ingested protein.

LONGENECKER, J. B. AND HAUSE, N. L. (E. I. du Pont de Nemours and Co., Wilmington, Del.). *Arch. Biochem. Biophys. 84*, 46–59 (1959).

Plasma amino acid changes of the adult dog after a meal have been found to be directly dependent upon the amino acid compn. of the protein ingested if it is postulated that the individual essential amino acids are removed from the blood by the body tissues at rates proportional to the amino acid requirements of the dog. A Plasma Amino Acid Ratio procedure is presented which permits the evaluation of the amino acid adequacy in a food protein for the nourishment of the animal species to which it is fed.

Quantitative nutritional studies with water-soluble chemically defined diets. VIII. The forced feeding of diets each lacking in one essential amino acid.

SUGIMURA, T., BIRNBAUM, S. M., ET AL. (Natl. Insts. of Health, Bethesda, Md.). *Arch. Biochem. Biophys. 81*, 448–54 (1959).

Diets free of histidine, tryptophan, lysine, phenylalanine, and threonine caused the animals to lose between 0.2 and 1.0 g./day over an 11-day period. Diets free of methionine, leucine, and isoleucine caused the animals to lose, 1–2 g./day. Most of the animals on these diets survived, and all the survivors gained when force-fed the complete diet. All the animals on the valine-free diet rapidly sickened and failed to survive beyond 9 days.

The effects of several milk components and similar compounds on the utilization of carotene by the rat.

RAICA, N., VAVICH, M. G. AND KEMMERER, A. R. (Univ. of Arizona, Tucson). *Arch. Biochem. Biophys. 83*, 376–80 (1959).

When 3.5% casein or 5% lactose, fructose, or galactose was added to carotene-water emulsion, no significant effect on carotene utilization was noted in rats fed 60 μg. carotene daily. When 3.5% gelatin or 0.5% lactalbumin or 5% glucose or raffinose was added, carotene utilization was significantly decreased.

Algae as a source of human food.

ANON. *Nutrition Revs. 17*, 238–40 (1959).

Studies have been conducted on the possibility of algae as a source of human food. It is concluded that algae do have nutritive value which could be applied to human nutrition. Objections noted are the cost of production and processing, the relative deficiency of certain vital nutrients such as methionine, the incomplete digestibility and poor acceptability due to odor, flavor, and color.

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INDUSTRY NEWS

A truck trailer, loaded October 1, 1959, with perishable foodstuffs and carried piggy-back on a Southern Pacific Railroad car from the Libby, McNeill & Libby quick-freezing plant in Sunnyvale, California, was unloaded in Chicago on the morning of October 7. The noteworthy features about this shipment are that conventional freeze methods were not applied to this food at Sunnyvale and also that no artificial refrigerants were necessary or added to the 40 foot trailer's perishable cargo while it was enroute for six full days as has had to be the case heretofore in the shipment of foods under ordinary refrigeration. This shipment was loaded into the trailer at 0° Fahrenheit at Sunnyvale. Thereafter liquid nitrogen, by a process known as **LIQUEFREEZE,** was pumped into the trailer body. The liquid nitrogen penetrated the food cartons and brought the temperatures of the food products down to many degrees below 0° Fahrenheit. A similar trailer owned by Acme Fast Freight, Inc., loaded in California with a larger assortment of Libby foods treated by the LIQUEFREEZE Process arrived at the Midwest Grocery plant here in Chicago after seven days in transit piggy-back by rail, exposed enroute to varying climatic conditions. When the trailer was opened, the food was found to average −35° Fahrenheit. Included in this shipment were such highly perishable items as strawberries and raspberries and a number of vegetables.

Both trailer bodies involved in these shipments were especially fitted out by the Haskelite Corporation of Grand Rapids, Michigan, with insulation patented by the the LIQUEFREEZE Corporation, New York, a subsidiary of Isbrandtsen Company, Inc., for utilization of the LIQUEFREEZE Process of freezing foodstuffs. This specialized insulation consists of a non-water absorbing material called polystyrene sandwiched between ⅜ inch plywood panels which in turn are spring-loaded into the trailer bodies to allow for thermo movement. The use of the LIQUEFREEZE Process in freezing foods for transport whether by truck, rail, sea or air has many marked advantages. Among these is the fact that no mechanical equipment is used or needed.

Expansion News

Foreign Importer Plans Expansion. A tea and vanilla importer in Western Germany plans to expand its product line to include American-manufactured food products. The organization is said to have been very familiar with the food provision and ice cream industries since before the turn of the century, and have an established and effective sales organization throughout Western Germany. In addition, they claim to be well placed to introduce new products in the food field, and are especially interested in ingredients for sale to food processors. For further information write the Executive Secretary, Institute of Food Technologists, 176 W. Adams, Chicago 3, Ill.

Two long-time supporters of FOOD TECHNOLOGY and experts in the food advertising field, **Edward G. Chase** and **C. Ralph Bennett** are now operating a new advertising agency at 241 East 58 Street, New York, N. Y. Called Bennett & Chase & Company, Inc., the new agency will handle the Vitamin Division and Aromatic Division of Hoffmann-La Roche, Inc., as well as Hoffmann-La Roche Ltd., Canada. In making this move, both men resigned from Fred Gardner Company, Inc., where Mr. Bennett was a founder, director, executive vice-president, and creative director, and Mr. Chase was vice-president and account executive for the agency's major accounts.

INDUSTRY PUBLICATIONS

Proctor & Schwartz, Inc. recently issued a new bulletin describing their **drying equipment, dehydrators, and freezing equipment.** Further information may be obtained by writing Proctor & Schwartz, Inc., at Seventh Street and Tabor Road, Philadelphia 20, Penna., and requesting Bulletin No. 447.

Carpenter Steel Company's **"super corrosion resistant" alloys** are described in their new bulletin, which contains tables showing comparative resistance of Hastelloy Alloys B and C to such corrosive media as hydrochloric, phosphoric and sulphuric acids. Workability, chemical analysis, and physical and mechanical properties of the two alloys are also described in the bulletin, which can be obtained from The Carpenter Steel Company, Alloy Tube Division, Union, N. J.

Early in November, Magnus, Mabee & Reynard, Inc., released their new and completely revised **36 page catalog containing well over 1000 entries** on essential oils, concentrated flavors, perfume oils, aromatic chemicals, oleorsins, and balsams. Six pages are devoted to Magna Concentrols for food products, and according to company objectives, the catalog is hoped to be the best publication of its kind in the field. For a copy, write Magnus, Mabee & Reynard, Inc., 16 Desbrosses Street, New York 13, N. Y.

PERSONNEL

Dr. William Allen Hamor, IFT member and Senior Director of Research, Mellon Institute, retired December 31, after more than a half-century of distinguished service to science. Long acknowledged to be one of the nation's leading research authors and editors, Dr. Hamor has been called "the greatest living American authority on the literature of chemistry." He is the author or co-author of nearly two hundred articles and publications, including five books. For his contributions to research management and the application of human relations to research, Dr. Hamor has received the following honorary degrees: D.Sc., University of Pittsburgh, 1935; Sc.D. Grove City (Pa.) College, 1932; Sc.D., Univer-

sity of Louisville, 1947, and LL.D., University of Miami (Fla.), 1947. In addition to IFT membership, Dr. Hamor belongs to twenty-three other organizations.

International Flavors & Fragrances Inc. announced today a further expansion of its Flavor Division here, and at the same time it was disclosed that **Henri van Mameren** had been named General Manager, and **Dr. James H. McGlumphy** Technical Director in charge of research, manufacturing, and product control. Prior to Mr. van Mameren's appointment, he served as Managing Director of the company's Paris subsidiary, as Assistant to the President in Holland, and as General Manager of a subsidiary in Brussels, Belgium. Dr. McGlumphy has been associated with the company for more than 25 years and is widely known throughout the industry, having served on many committees and as an advisor to the U. S. Government and the armed forces.

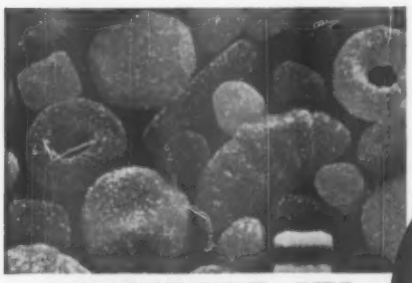
J. H. McGlumphy

Dr. Edward A. Nebesky has joined the staff of the Food Science Department at Rutgers University as professor of food science. He had previously taught at Cornell and the University of Massachusetts. "Because of Dr. Nebesky's extensive background in packaging he is ideally suited to head up much of the work we are planning in the field of packaging," says Dr. Roy E. Morse, chairman of the Department of Food Science at Rutgers. Dr. Nebesky has had experience in packaging as product manager in The Cryovac Company of Cambridge, Mass.

E. A. Nebesky

IN MEMORIAM

Walter Joseph Murphy, Editorial Director of the American Chemical Society's Applied Journals, died on November 26, 1959, in Washington, D. C. Dr. Murphy was an able, resourceful person who contributed in major degree to the growth and influence of the ACS publications, particularly those devoted to industrial problems in the chemical field. From 1921, when he was graduated with a bachelor of science degree in chemistry from the Polytechnic Institute of Brooklyn, on to his death last November, his interests were centered on chemistry. He served the profession he had elected to enter in innumerable ways—as editor, organizer and manager of the ACS News Service, representative on foreign scientific missions, and as



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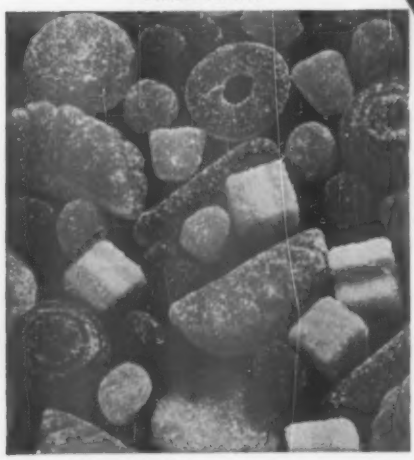

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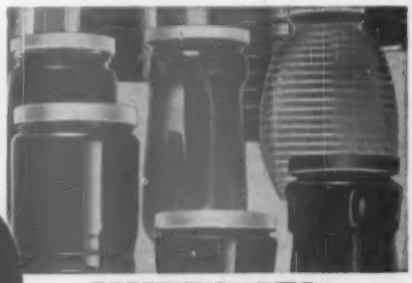

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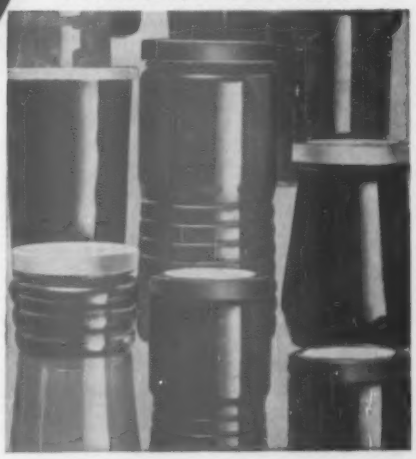

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an advisor to various Government scientific agencies, notably the AEC and the Chemical Corps. He was active in almost every phase of the ACS program and his influence was felt in councils on chemical education, in Government research and development, and, in industry—in fact, throughout the scientific community. His distinguished career has ended but all technical groups have benefited and will continue to benefit by his dynamic efforts to increase the stature of professional workers not alone in chemistry but in all fields of science and technology.

Dr. Howard D. Brown, for many years professor of horticultural products at Ohio State and nationally-known as an educator, author and scientist, died September 29, 1959, at his home in Worthington, Ohio. Dr. Brown was born on a farm near Lexington, Ill., on Dec. 7, 1891 and reared in that vicinity. He attended the University of Illinois and received his bachelor of science degree in 1914 and the master of science in 1917. For a short time in 1921, he attended the University of Wisconsin, and in 1926 went to Michigan State to earn his doctor of philosophy degree a year later. He began his professional career as an instructor at the University of Illinois in 1914. In 1918 he served in France as an officer in the U. S. Army Quartermaster Corps. In 1919 he joined the staff of Purdue University as an associate professor of vegetable gardening. Dr. Brown transferred to Ohio State University in 1929 and remained at that institution until his retirement in 1957. After 1957 he was Research Coordinator for the Potato Chip Institute.

H. D. Brown

Dr. Brown developed and improved the Indiana Baltimore tomato, which at one time was used on approximately two-thirds of the canning crop acreage of the United States. He also developed the so-called "unit system" of soil sterilization to free soil from injurious insect and disease pests. His researches dealt with a wide variety of subjects, including: greenhouse fumigation and ventilation, vegetable pruning, potato apical dominance, strain and variety tests, irrigation, processing vegetables and fruits, hydroponics, vegetable breeding and many others.

For his outstanding accomplishments, he was the recipient of the second annual C. W. Kelsey award from the Vegetable Growers Association of America. Dr. Brown was the author of more than 70 scientific publications and co-author of two books, *Frozen Foods, Processing and Handling*, 1946, and *Vegetable Science*, 1949.

He was active in many national and local organizations, including: Vegetable Growers Association of America (secretary from 1933 to 1954), National Association of Hot House Vegetable Growers (secretary-treasurer from 1940 to 1945) and the American Society for Horticultural Science (vice president in 1938). Scientific organizations to which he belonged included the American Society for Advancement of Science, American Society for Horticultural Science, American Society of Plant Physiologists, the Institute of Food Technologists and the Ohio Academy of Science.

He is survived by his widow, Elsie Stillwell Brown.

John Edward Nicholas, 722 Holmes Street, State College, Pennsylvania died unexpectedly while vacationing at Sagamore Beach, Massachusetts, September 15, 1959. Mr. Nicholas professor emeritus of agricultural engineering, retired July 1, 1958, after serving on the Penn State faculty nearly 30 years.

J. E. Nicholas

Mr. Nicholas, attended Lehigh University where he received the degree of mechanical engineering in

1915. In 1926, he was awarded the master of science degree by Massachusetts Institute of Technology. He served as a mechanical engineer with Bethlehem Steel Corporation from 1915 to 1921 and then served on the faculty of the University of Illinois, Rice Institute, Massachusetts Institute of Technology, and University of Minnesota before his appointment at Penn State in 1929. His work at Penn State was concerned with the processing of food products and he published more than 100 papers on his work. He was widely known for his research in the freezing of food, and also on milk cooling.

He was a fellow of the American Society of Refrigeration Engineering and also the American Society of Agricultural Engineers. He was a member of the American Institute of Electrical Engineers, Institute of Food Technologists, American Society for Engineering Education, Society of the Sigma Xi, and Gamma Sigma Delta, agricultural honor society.

Born June 20, 1893, in Eckley, Pennsylvania, he was the son of Michael and Barbara Kasha Nicholas. He was married in 1925 to Mildred W. Carpenter who survives with three sons, Richard C. Nicholas, East Lansing, Michigan; Dr. W. Channing Nicholas, Bismark, North Dakota; and Bruce O. Nicholas, Harrisburg, Pennsylvania.

Ernest William ("Bob") Hicks, officer-in-charge of the physics section in the Division of Food Preservation of the Australian Commonwealth Scientific and Industrial Research Organization, died in Sydney on November 2nd after a short illness. He was 52 years of age.

E. W. Hicks

Hicks was a graduate of the Arts and Science faculties of the University of Melbourne, with major interests in mathematics and physics. After a period of research work on the ripening and transport of bananas, he had two years of post-graduate research experience at Cambridge (England). It was here that he developed the interest in the application of physics and mathematics to the problems of food science, which he was to use so successfully during the next 20 years.

Hicks had a complete mastery of the mathematics of heat transfer and of diffusion, which he put to highly effective use in analyses of the simultaneous transfer of heat and moisture from foodstuffs during cooling and storage, in the prediction of the performances of refrigerated rail and road vehicles and in analyses of the heat processing of canned foods. In the latter studies, published mainly in IFT Journals, Hicks introduced several new concepts which have led to more precise estimates of bactericidal effects and to a much better understanding of the factors influencing sterilization.

The C.S.I.R. O. Division of Food Preservation has lost a great leader whose influence extended far beyond his own research team.

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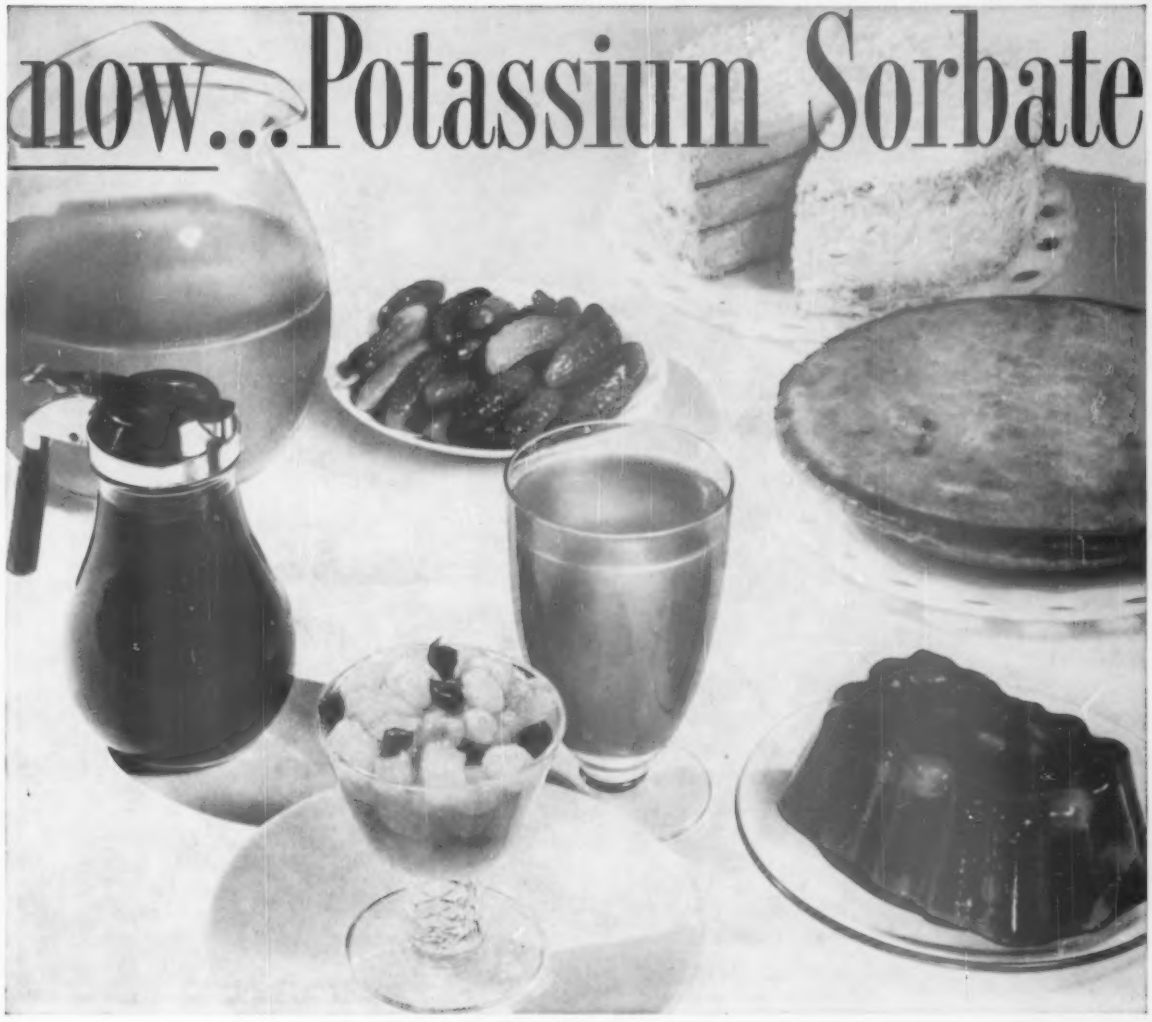

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